MACAN CapStone Conference

April 20-26, 2013
Dan Carmel Hotel, Haifa & HaGoshrim Hotel, Israel
It is the goal of MACAN to establish an environment conducive to promoting communication and collaboration between groups using thermodynamic approaches with groups studying the atomistic structure of interfaces, since bridging this particular scientific gap has the potential to generate new design criteria for advanced material systems. The project is based on a core group of European partners, augmented by experts in the field from Japan, the US, India, and Brazil. The MACAN partners have realized that such a form of communication is critical to advancing the field of interface science and interface-based technology. The core group of partners has established structured vehicles for discussion and dissemination of knowledge via workshops, a summer school, and via scientific exchange between experts in Europe, Japan, the US, India and Brazil. These meetings were open to the general European public, and identifying additional European and non-European experts was one of the main goals of the general program. While the core group of partners is academic, European industry is involved in the structured discussions to facilitate identification of key interface-related industrial issues, and to promote transfer of knowledge from the academic environment to European industry.

CapStone is the concluding MACAN conference, based on invited presentations by leading scientists in the field. While originally intended as a partner meeting, the core leaders of MACAN decided to expand CapStone to include non-partners as part of the dissemination action of MACAN. CapStone is divided into two parts. The first part of the meeting is based primarily on invited speakers who are not Macan partners, augmented by selected MACAN speakers. In addition, following the philosophy of MACAN, oral sessions will be summarized by discussion sessions led by MACAN young scientists with the goal of bridging the gap between continuum and atomistics of interfaces. The discussion sessions will provide MACAN young scientists scientific exposure, which is also a goal of the program. This will take place from Saturday April 20th through Wednesday morning April 24th at the Dan Carmel Hotel in Haifa. On Wednesday morning the MACAN partners and their students will proceed to the HaGoshrim Hotel for a closed meeting based on presentations by young scientists, and a concluding discussion of the outcome of MACAN.
### MACAN CapStone Program

**Saturday, April 20th:**
Arrival to the Dan Carmel Hotel in Haifa, with a reception at 20:00 for all guests.

**Sunday, April 21st:** General Program (King David Hall):

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<tr>
<th>Time</th>
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<td>09:00 – 09:30</td>
<td>D Chatain, WD Kaplan</td>
<td>The Goals &amp; Achievements of MACAN</td>
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<td>France, Israel</td>
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<tr>
<td>09:30 – 10:10</td>
<td>Avi Marmur</td>
<td>Wetting Equilibrium: Macroscopic Effects of Micro- and Nano-Features</td>
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<td>Technion, Israel</td>
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<td>10:10 – 10:50</td>
<td>Marie-Laurence Giorgi</td>
<td>Influence of Ferrite Grain Orientation on the Formation of Selective Oxide Particles</td>
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<td>École Centrale Paris, France</td>
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<td>10:50 – 11:20</td>
<td><strong>Coffee Break</strong></td>
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<td>11:20 – 12:00</td>
<td>Greg Rohrer</td>
<td>The Relationship between Grain Boundary Energy Anisotropy and Grain Boundary Complexity Transitions</td>
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<td>Carnegie Mellon University, USA</td>
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<tr>
<td>12:00 – 12:40</td>
<td>Yuichi Ikuhara</td>
<td>Atomic Structures and Chemical Bonding State of Grain Boundaries with Dopant Segregation</td>
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<td>The University of Tokyo, Japan</td>
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<td>Carnegie Mellon University, USA</td>
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<tr>
<td>13:30 – 14:30</td>
<td><strong>Lunch</strong></td>
<td>Dan Carmel Hotel</td>
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<td>14:30 – 15:10</td>
<td>Uli Dahmen</td>
<td>Observation and Analysis of Grain Boundary Motion in 90° &lt;110&gt; Bicrystals from the Nanometer to the Atomic Scale</td>
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<td>Lawrence Berkeley National Laboratory, USA</td>
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<td>15:10 – 15:50</td>
<td>Jorg Weissmüller</td>
<td>Grain Rotation at the Nanoscale</td>
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<td>Technische Universität Hamburg-Harburg, Germany</td>
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<td>15:50 – 16:20</td>
<td><strong>Coffee Break</strong></td>
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<td>16:20 – 17:00</td>
<td>Rishi Raj</td>
<td>Roles of the Interfacial ElectroChemicalMechanical Potential, and of the Particle Size, in the SPS Process</td>
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<td>University of Colorado at Boulder, USA</td>
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<tr>
<td>17:00 – 17:40</td>
<td>Klaus van Benthem</td>
<td>In situ Transmission Electron Microscopy Characterization of Interfaces under Externally Applied Stress Fields</td>
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<td>University of California, Davis, USA</td>
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<td>17:40 – 18:30</td>
<td><strong>Young Scientists</strong></td>
<td>Discussion Session</td>
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<td>19:00</td>
<td><strong>Dinner</strong></td>
<td>Departure to the Druze Village from Hotel Lobby</td>
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Monday, April 22\textsuperscript{nd}, General Program (King David Hall):

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<tr>
<td>08:30 – 09:10</td>
<td>John Blendell (\textit{Purdue University, USA})</td>
<td>Motion and Shear of Faceted Grain Boundaries</td>
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<tr>
<td>09:10 – 09:50</td>
<td>Frances Ross (\textit{IBM, USA})</td>
<td>Dynamics at the Growth Interface During the Formation of Semiconductor Nanowires</td>
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<td>09:50 – 10:30</td>
<td>Christoph Koch (\textit{Ulm University, Germany})</td>
<td>Using Dynamically Scattered Electrons for Retrieving 3D Atomic Positions in Nanoparticles</td>
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<td>10:30 – 11:00</td>
<td>Coffee Break</td>
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<tr>
<td>11:00 – 11:40</td>
<td>Etienne Snoeck (\textit{CNRS Toulouse, France})</td>
<td>Mapping Nanofields by Electron Holography</td>
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<tr>
<td>11:40 – 12:10</td>
<td>Tom Kelly (\textit{CAMECA Instruments, Inc., USA})</td>
<td>Toward Atomic-Scale Tomography</td>
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<tr>
<td>12:10 – 13:00</td>
<td>Young Scientists</td>
<td>Discussion Session</td>
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<td>13:00 – 14:30</td>
<td>Lunch</td>
<td>Dan Carmel Hotel</td>
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<td>14:30 –</td>
<td>Informal Networking Opportunities</td>
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<tr>
<td>18:00</td>
<td>Dinner</td>
<td>Akko (Departure from hotel lobby)</td>
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**Tuesday, April 23rd, General Program (King David Hall):**

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<thead>
<tr>
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<tbody>
<tr>
<td>08:30 – 09:10</td>
<td>Mike Finnis</td>
<td>The Growth of Alumina Scales on High Temperature Structural Alloys</td>
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<tr>
<td>09:10 – 09:50</td>
<td>Mike Gandman</td>
<td>Pt Precipitates in Polycrystalline Alumina: A Model System for Investigation of Metal Equilibration in Ceramics</td>
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<tr>
<td>09:50 – 10:30</td>
<td>Rolf Janssen</td>
<td>Synthesis of Advanced Metal-Ceramic Composites via Controlled Interface reactions</td>
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<td>10:30 – 11:00</td>
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<td>Coffee Break</td>
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<tr>
<td>11:00 – 11:40</td>
<td>Eva Olsson</td>
<td>Correlation between Structure of Interfaces and Active Sites and Aging Properties of Noble Metal Catalyst Particles on Oxide Supports</td>
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<tr>
<td>11:40 – 12:10</td>
<td>Carol Handwerker</td>
<td>Stress Relaxation in Tin Thin Films: From Whiskers to Grain Growth</td>
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<td>12:10 – 12:50</td>
<td>Yuri Mishin</td>
<td>Interface Thermodynamics under Mechanical Stresses: Theory and Atomistic Modeling</td>
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<td>13:00 – 14:30</td>
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<td>Lunch                                      Dan Carmel Hotel</td>
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<tr>
<td>14:30 – 15:10</td>
<td>Vikram Jayaram</td>
<td>Measuring Fracture Toughness Gradients in Pt-Ni-Al Bond Coats with Micron-Scale Spatial Resolution</td>
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<td>Coffee Break</td>
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<tr>
<td>16:30 – 17:10</td>
<td>Izabela Szlufarska</td>
<td>Toward Computational Design of Wear Resistant Materials: Molecular Understanding of Friction</td>
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<td>Discussion Session</td>
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<td>18:00 – 18:30</td>
<td>W Kaplan, D Chatain</td>
<td>Concluding Remarks</td>
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<td>20:00</td>
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<td>Gala Dinner                                Rondo in the Dan Carmel Hotel</td>
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<td>09:00</td>
<td>Macan partners depart by bus for HaGoshrim</td>
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<td>Lunch at Bat Ya’ar</td>
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<td>15:30 – 16:30</td>
<td>Arrival and Check-In</td>
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<td>16:30 – 17:15</td>
<td>Sandra Drev&lt;br&gt;Jožef Stefan Institute, Ljubljana, Slovenia&lt;br&gt;Lectures in Oren Hall&lt;br&gt;Electron Microscopy Study of Twinning and Formation of Modulated Structures in Be-Doped MgAl$_2$O$_4$ Spinel</td>
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<td>17:15 – 18:00</td>
<td>Burcu Öğüt&lt;br&gt;Max-Planck-Institute for Intelligent Systems, Stuttgart, Germany, Germany&lt;br&gt;Toroidal Plasmonic Eigenmodes in Oligomer Nanocavities for the Visible</td>
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<td>18:00 – 18:45</td>
<td>Francesco Colonna&lt;br&gt;Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany&lt;br&gt;Multiscale Simulations of Grains and Grain Boundaries in Silicon Nitride</td>
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<td>18:45 – 20:00</td>
<td>MACAN Students&lt;br&gt;3 Minute Poster Presentations</td>
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<td>20:00 – 21:00</td>
<td>Dinner&lt;br&gt;HaGoshrim</td>
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<tr>
<td>21:00 – 23:00</td>
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Thursday, April 25th, General Program: (Oren Hall, HaGoshrim)

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<td>08:30 – 09:15</td>
<td>Hannes Guhl</td>
<td>Modeling Grain Boundaries in Al₂O₃ based on DFT</td>
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<td></td>
<td>Imperial College</td>
<td>London, UK</td>
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<tr>
<td>09:15 – 10:00</td>
<td>Peter Krogstrup</td>
<td>Crystal Growth Dynamics of III-V Nanowires via the VLS Mechanism</td>
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<td>Niels Bohr Institute,</td>
<td>University of Copenhagen, Denmark</td>
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<td>Ludwig-Maximilians-</td>
<td>University München, Germany</td>
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<td>Forschungszentrum</td>
<td>Jülich, Germany</td>
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<td>12:00 – 12:45</td>
<td>Praveen Kumar</td>
<td>Electromigration-Assisted Interfacial Sliding at Hetero-Interfaces</td>
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<td>Indian Institute of</td>
<td>Science, Bangalore, India</td>
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<td>Lunch</td>
<td>HaGoshrim</td>
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<td>14:30 – 15:15</td>
<td>Dor Amram</td>
<td>Phase transformations in thin Au(Fe) films and Au(Fe) particles on a sapphire substrate</td>
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<td>Technion, Israel</td>
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<td>15:15 – 16:00</td>
<td>Akiho Nakamura</td>
<td>Phase Distribution and Strain Analysis of LiFePO₄ / FePO₄ Interface by HAADF STEM Imaging</td>
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<td>The University of</td>
<td>Tokyo, Tokyo, Japan</td>
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<td>16:00 – 16:30</td>
<td>Coffee Break</td>
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<tr>
<td>16:30 – 17:15</td>
<td>Rachel V. Zucker</td>
<td>A Model for Solid State Dewetting of a Fully-Faceted Thin Film</td>
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<td>MIT, Cambridge, USA</td>
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<td>17:15 – 18:00</td>
<td>Ece Alpaslan</td>
<td>Deducing the Role of Functionalizing Macromolecules in the Nucleation of Colloidal Nanoparticles</td>
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<td>Turkey</td>
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<td>18:00 – 18:30</td>
<td>Simon van Dam</td>
<td>European Research &amp; Innovation Policy Aspects of MACAN</td>
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<td>Israel</td>
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<td>18:30 – 19:00</td>
<td>Bridging the Gap</td>
<td>Partners, Led by WD Kaplan &amp; D Chatain</td>
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<td>19:00 – 22:00</td>
<td>Dinner</td>
<td>Dag Al HaDan</td>
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<td>22:00</td>
<td>Wetting Experiments</td>
<td>HaGoshrim Pub</td>
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Friday, April 26th, General Program
09:00  Departure by bus for Haifa
Invited Abstracts
Wetting Equilibrium:
Macroscopic Effects of Micro- and Nano-Features

Abraham Marmur

Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Wetting equilibrium, as characterized by the equilibrium contact angle, is a macroscopic expression of micro- and nano-features of the solid surface. This important information can be applied in two ways: (a) bottom-up approach - controlling macro-phenomena by designing the micro-features of the solid; and (b) top-down approach - characterizing the solid surface by proper measurement of the apparent contact angle. The proper methodology for measuring contact angles is described, followed by a discussion of its limitations, on the one hand, and possible interpretation, on the other. The bottom-up approach is presented with regard to the design of non-wettable surfaces in air and under water (super-hydrophobicity/hygrophobicity).

References
Influence of Ferrite Grain Orientation on the Formation of Selective Oxide Particles

Marie-Laurence Giorgi\textsuperscript{1}, Nathalie Ruscassier\textsuperscript{1}, Amélie Ollivier\textsuperscript{1}, Si Chen\textsuperscript{1}, Paul Haghi-Ashtiani\textsuperscript{2}, and Grégory Geneste\textsuperscript{3}

\textsuperscript{1}Laboratoire de Génie des Procédés et Matériaux
\textsuperscript{2}Laboratoire de Mécanique des Sols, Structures et Matériaux, CNRS-UMR 8579
\textsuperscript{3}Laboratoire Structures, Propriétés et Modélisation des Solides, CNRS-UMR 8580
École Centrale Paris, Châtenay-Malabry, France

Before hot-dip galvanizing, the steel sheets are annealed in an atmosphere of N\textsubscript{2} and H\textsubscript{2}, containing only traces of water (about -30°C dew point). The main purposes of this heat treatment are to recrystallize the steel substrate after cold rolling and to reduce the iron oxides in order to improve the wettability by liquid zinc. At the same time, the less-noble alloying elements (Mn, Si, P, Cr, Al) of the steel preferentially oxidize and segregate to the surface. The steel surface is then partly or wholly covered by oxide particles (figure 1), sometimes resulting in problems of wettability by liquid zinc [1].

The present study will focus on the nucleation and growth of the oxide particles formed on the surface of an \textit{IF Ti} steel (Table 1) and a Fe-Mn (1 wt.%\%) binary alloy. The samples were annealed by means of a laboratory furnace with a temperature profile relevant to galvanizing line practice. The sample is first heated to 800°C at a rate of approximately 6°C s\textsuperscript{-1}. It is kept at that temperature for 60 s before being cooled to room temperature. The parameters characteristic of the oxide particles are then determined using several analysis techniques: Field Emission Gun Scanning Electron Microscope, Transmission Electron Microscope and Electron Diffraction, X-ray Photoelectron Spectroscopy.

In the case of the \textit{IF Ti} steel, when the annealing temperature increases, the alloying elements Mn, Si, Al and B diffuse towards the surface where they oxidize. Oxides are composed of MnO, Mn\textsubscript{2}SiO\textsubscript{4} (or MnSiO\textsubscript{3}) and/or MnAl\textsubscript{2}O\textsubscript{4}, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and B\textsubscript{2}O\textsubscript{3}. Oxide nucleation mainly occurs between 650°C and 750°C on preferential sites such as grain boundaries and sub-boundaries of the ferrite on the recrystallization process and the facets formed on the ferrite during annealing. The growth of the oxides that have nucleated is then observed. During annealing, from 750°C, the surface density of the oxides decreases while their size increases. Growth seems to be coupled with coalescence and possibly with Oswald ripening [2]. The surface density and the size of the oxide particles strongly depend on the orientation of the ferrite grains, as shown in figure 2 in the case of two ferrite grain orientations.

In order to simplify and to better target the problem, we then focused on the selective oxidation of the Fe-Mn (1 wt.%\%) binary alloy. In this case, the oxide particles formed are composed of MnO only. As for the steel studied, the surface density and the size of the oxide particles depend on the orientation of the ferrite grains. The morphology of the oxide particles is also found to be very different from one ferrite grain orientation to the other (figure 3).
Table 1: Average composition of the IF Ti steel studied (wt.%)

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<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
<th>B</th>
<th>S</th>
<th>N</th>
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<td>0.005</td>
<td>0.074</td>
<td>0.450</td>
<td>0.034</td>
<td>0.049</td>
<td>0.034</td>
<td>0.072</td>
<td>0.005</td>
<td>0.012</td>
<td>0.0047</td>
<td>0.003</td>
<td>0.002</td>
<td>0.025</td>
<td>0.033</td>
<td>0.008</td>
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Figure 1: IF Ti steel surface covered by nanometric oxide particles after annealing.

Figure 2: Influence of the ferrite grain orientation on the size and surface density of the oxide particles in the case of the IF Ti steel, the surface density is larger on the (100) ferrite grain (left-hand side image) than on the (111) ferrite grain (right-hand side image).

Figure 3: Influence of the ferrite grain orientation on the size, surface density and morphology of the oxide particles in the case of the Fe-Mn binary alloy, the morphology of the oxide particles strongly depends on the ferrite grain orientation.

References
The Relationship between Grain Boundary Energy Anisotropy and Grain Boundary Complexion Transitions

Stephanie A. Bojarski and Gregory S. Rohrer

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

The recent discovery that the structure and composition of grain boundaries can abruptly change, leading to discontinuous changes in grain boundary properties, such as energy and mobility, provides a key piece of information that helps to explain abnormal grain growth [1]. In this talk, I will first review experimental evidence that complexion transitions in bulk ceramics lead to a decrease in the grain boundary energy, using data from alumina and yttria [2-4]. For example, the data in Fig. 1 shows the relative energies of grain boundaries in Nd$_2$O$_3$ doped alumina. Lower energy grain boundaries are found around the largest grains, which have a bi-layer of segregated Nd; the grain boundaries around smaller grains have a monolayer of Nd and a higher relative grain boundary energy.

Based on this evidence, we hypothesize that grain boundary complexion transitions preferentially nucleate at high-energy grain boundaries and that it is a continuous nucleation process. Experiments to test this hypothesis have been conducted by sandwiching doped alumina between single crystals of sapphire with different and known orientations. The differently oriented crystals create characteristically different average grain boundary energies with the powder. After initial consolidation, the relative grain boundary energies are evaluated by the thermal groove method. The sample is then annealed in the temperature range where a complexion transition is known to occur. Subsequent characterization of the microstructure suggests that the complexion transition occurs preferentially at the higher energy grain boundaries, in support of the hypothesis. The images in Fig. 2 show an example of one of the experimental outcomes, where grains near the higher energy r-terminated interface have grown farther.

Finally, recent observations also suggest that the complexion transitions may nucleate heterogeneously at grain boundaries connected to those that have already transformed. Measurements of the grain boundary energy in 100 ppm Ca-doped yttria indicate that boundaries around abnormally large grains and the small adjacent grains have a lower energy than small grains much further away. The higher energy grain boundaries are associated with a complexion that has a bilayer of adsorbed Ca and the lower energy boundaries are associated a complexion that consists of an amorphous intergranular film. The measurements suggest that the intergranular film extends beyond the periphery of the largest grain, but not throughout the entire sample.
Figure 1: Cumulative distribution of dihedral angles in (a) neodymia-doped alumina annealed at 1400 °C with normal (complexion I) and abnormal (complexion III) grain boundaries. Insets schematically illustrate the boundary structure of the two complexions [4].

Figure 2: EBSD maps of a cross section of a sandwich sample after consolidation. On the left, a single crystal of sapphire with the r-plane in contact with 60 ppm Ca-doped Al₂O₃. On the right, a single crystal of sapphire with the C-plane in contact with the same 60 ppm Ca-doped Al₂O₃. The grains are colored by their orientation perpendicular to the plane of the image, according the legend below.

References
Atomic Structures and Chemical Bonding State of Grain Boundaries with Dopant Segregation

Yuichi Ikuhara\textsuperscript{1,2,3}

\textsuperscript{1}Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
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Doping oxide materials with impurity ions have been a widespread technique for altering the properties of materials. In many cases, a macroscopic change is apparently observed, but characterizing the changes of the structure of the materials on the atomic scale remains a difficult task. Particularly in the case of oxides, it is widely assumed that the dopants segregate to crystal defects (e.g. dislocations and grain boundaries (GBs)), as they are known to be sinks for impurity segregation. Recently, some studies have been performed on unraveling the atomic scale mechanism of dopant segregation to defects in GBs in oxides \cite{1,2}. But, these researches have been mainly performed for the simple model GB with isovalent dopants w.r.t. the grain matrix. Because the number of oxides and possible impurities are very large, a wide range of oxide systems must be characterized to fully understand the segregation behavior at GBs in oxides.

In this study, complex dopants systems with aliovalent dopants and co-dopant are quantitatively investigated by combining high resolution scanning transmission electron microscopy (STEM) characterization and first principles calculations. For the model GB with the aliovalent dopants, Zr\textsuperscript{4+}-doped Al\textsubscript{2}O\textsubscript{3} were selected for the investigation. For the co-dopant system, Ca and Ti co-doped GB were characterized. It is interesting to confirm how the charge neutrality is compensated at the GBs in such systems to relax the atomic structures. To accomplish this, two single crystals of Al\textsubscript{2}O\textsubscript{3} and MgO were cut to have the suitable misorientation for $\Sigma$31 and $\Sigma$5 grain boundaries $\cite{1,3}$, respectively. The two single crystals were joined using diffusion bonding. For characterization, Cs-corrected STEM (JEM-2100F, JEM-ARM200F, JEOL Co. Tokyo Japan) was used to acquire high-resolution high-angle annular dark-field (HAADF) STEM images.

Fig.1 (a) shows HAADF STEM image of the Zr doped Al\textsubscript{2}O\textsubscript{3} $\Sigma$31 tilt grain boundary. It is found that periodic structural units formed along the grain boundary plane consist of a seven-membered ring of cation columns, as well as a deformed “peanut-shaped” unit, also consisting of seven cation columns (Fig.1(b)). As can be seen in (b), bright columns along the grain boundary plane correspond to Zr ions, and the dark sites indicated by black triangles may correspond to the Al vacancy sites. Using first principles for these systems, the segregation energy was estimated by comparing the defect formation energy at the GB with that at the bulk. It was found that the segregation energy is relatively high for all cases without introducing vacancies. Following these calculations, four key Zr segregation sites were picked to investigate the segregation energies of the Zr substitution with an associated Al vacancy defect pair by keeping each Zr substation site the same but changing the location of the neighboring Al vacancy. It was found that the segregation of Zr\textsuperscript{4+} is stabilized by associating $V_{\text{Al}}$\textsuperscript{3-}.

Fig.2(a) shows HAADF STEM image of Ca and Ti co-doped $\Sigma$5 GB in MgO. It can be seen that strong pair contrast is present along the GB, which is considered to correspond to Ca columns. It is also found that there are periodic spots with much weaker image contrast as indicated by the arrows. To understand this segregation behavior, first principles calculations were performed for the Ca and Ti segregated $\Sigma$5 GBs. It was found that the stability of the GB is enhanced by introducing Ca and
Ti simultaneously, which periodically segregate to the GB as shown in Fig.3 (b). To investigate whether Ti segregation and associated Mg vacancies can be responsible for the contrast variation, preferred sites for Ti were examined in all of its possible charge states. Geometrical investigation into the stable GB revealed a structural transformation: Ca ions in the left of pair spots relax laterally towards an interstitial sites indicated by the arrows in Fig. 3(b). The driving force for such a displacement is the adjacent Mg vacancies on both sides of GB plane, which frees up the space for Ca to relax into a more stable site, reducing substantially the GB free energy.

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Figure 1: (a) shows HAADF STEM image of the Zr doped \(\Sigma 31\) tilt grain boundary. (b) shows the same image with an overlay indicating the structural units along the grain boundary. (c) shows the same image with an overlay indicating the name of sites.

Figure 2: (a) HAADF STEM image of the \(\Sigma 5\) GB viewed from the [001] directions, indicating that there are the weak spots in addition to the two strong spots of Ca columns. (b) Most stable grain boundary atomic structures calculated for for Ca and Ti segregation.

References
Relation Between the Anisotropies of Interfacial Segregation and Interfacial Energy, and its Effects on the Equilibrium Crystal Shape of Alloys

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A multi layer nearest neighbor bond model of segregation at surfaces has been exercised to investigate the anisotropy of interfacial segregation (or adsorption). Cross-overs in segregation as a function of temperature, for interfaces of different orientation, have been previously observed experimentally for both surfaces and grain boundaries. This phenomenon had been interpreted as being the result of an entropy compensation effect. However, our modeling results rule out this interpretation. Furthermore, conventional wisdom has it that segregation should be stronger at higher energy interfaces, but this view is also not supported by our calculations.

In addition, the model has been used to investigate the effects of surface segregation on the equilibrium crystal shape (ECS) of alloys. Although nearest neighbor bond models can predict the existence of cusps at (100) and (111) surfaces, we still show that the appearance of other cusps in the γ-plot only occurs when the elastic strain energy contributions to the energy of segregation are finite. Cusps at orientations other than (111) and (100) can produce new facets on the ECS, but only in the temperature range close to the minima of γ(hkl)/γ(111) and/or γ(hkl)/γ(100). By searching the parameter space of the model, conditions have been found that lead to stabilization of (110), (311), (331) and (210) facets. These results are consistent with experimental observations on fcc alloys, where these facets have been observed. In addition, (320) and (530) facets which are not predicted by the model have been observed experimentally. These lie close to (210) along the [100] zone, and their presence could be due to surface reconstructions that the model is unable to account for.
Observation and Analysis of Grain Boundary Motion in 90° <110> Bicrystals from the Nanometer to the Atomic Scale

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We have investigated the mechanism and dynamics of grain boundary migration driven by capillary forces via in-situ electron microscopy, complemented by molecular-dynamics simulations. Using thin films of Au with the mazed bicrystal geometry we observed the shrinkage of island grains with 90° <110> tilt grain boundaries by diffraction contrast and high resolution imaging [1]. As shown in figure 1, the grains remained cylindrical throughout the shrinkage, and there was no measurable grain rotation even at very small sizes. The rate of shrinkage was found to be erratic and inconsistent with parabolic kinetics, accelerating before complete disappearance. Invariably, residual defects were found immediately after complete shrinkage, although the type and magnitude of the defects was different from grain to grain. An example of these defects is seen in figure 1d.

Figure 1: Still frames from an in-situ video recording showing grain shrinkage at 311°C. Due to the large sample tilt, the cylindrical island grain appears in an inclined projection, as outlined schematically in (a). The last 3 frames are 1/30 s apart, indicating that the grain remains strictly cylindrical throughout the shrinkage. Complete disappearance leaves defects (d).

Measurement of the grain boundary shape anisotropy showed a preference for facets on low-index planes of the crystals, including the mirror-symmetry planes of the bicrystal. These characteristic facets are shown at high resolution in figure 2, where the three characteristic facets are labeled A, B and C. The dynamics of boundary motion were found to be limited by nucleation and propagation of steps on these facets.

The cylindrical geometry and size of the experimentally observed island grains allowed direct comparison with molecular-dynamics simulations on the same length scale, which reproduced many of the experimentally observed features, including non-parabolic shrinkage, absence of systematic grain rotation, step-controlled migration, and dislocation debris after complete grain shrinkage. An island grain during shrinkage in a molecular dynamics simulation, shown in figure 3, demonstrates the tendency for faceting and the controlling role of C-type facets during grain boundary motion.
Figure 2: Anisotropy of grain boundary structure. (a) High resolution view of a typical boundary during in-situ shrinkage at about 300°C containing all three major inclinations (labeled A, B, C). (b) Atomic resolution view of island grain bounded mainly by B-type facets, before complete shrinkage.

Figure 3: Left: snapshot from MD simulation with initial grain diameter of 30 nm at $T/T_m = 0.46$. Note tendency for faceting and step in right vertical facet. Right: sequential grain boundary positions seen as concentric outlines of decreasing area. The four outermost outlines show how the vertical C-facets remain almost stationary for a period of 15 ns, followed by sudden fast motion after the right vertical facet disappears.

This presentation will illustrate the dynamic behavior of shrinking island grains and highlight the mechanisms that control interface motion. Differences between model and experiment will be discussed in terms of the possible role of impurities, surfaces and interfacial steps [2].

References
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Grain Rotation at the Nanoscale

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The process of grain rotation has long been studied due to its impact on sintering and on the plasticity of metals and ceramics, specifically at elevated temperature and/or under conditions of superplastic deformation. Grain rotation involves atomic rearrangements at grain boundaries, including transport on the scale of the grain size. The process is therefore accelerated – strongly, as it turns out – when the grain size is reduced. Not surprisingly, the contribution of grain rotation to the plastic deformation of polycrystals with a nanometer-scale grain size ("nanocrystalline materials") is a topic of current research. In the same context, the most fundamental driving force for grain rotation – namely the misorientation-dependent grain boundary excess free energy – might itself exhibit a size-dependence. Since the grain boundary excess free energy is large in nanocrystalline materials, its conceivable size dependence would have significant ramifications for the material’s thermal stability. This presentation will discuss the rotation of small grains, with an emphasis on the driving force and on the ensuing kinetics.

The talk is based on our recent discrete dislocation study of the untwisting of finite-site, small angle tilt grain boundaries [1]. That study investigates the kinetics of grain rotation in a bicrystal with a tilt grain boundary by studying the relaxation of an edge dislocation wall in a discrete-dislocation approach. The boundary is infinitely extended in one direction and of finite size in the orthogonal one. The relaxation process is simulated numerically by solving the equations of motion of the dislocations, assuming climb by diffusive transport in the boundary plane.

Surprisingly, we find that boundaries never rotate all the way into coincidence. Instead, the final state is a metastable array with 18 dislocations and, hence, with a finite misorientation that depends on the boundary length and the Burgers vector. The relaxation time to reach this metastable configuration is found proportional to the logarithm of the number of dislocations and to the cube of the length of the boundary. All boundaries with fewer than 18 dislocations are also metastable.

The metastability can be traced back to a repulsive action of the effective image forces on the leading dislocation in the array. This finding is surprising, since textbook knowledge has it that image forces on dislocations near free surfaces are universally attractive. It turns out that the repulsive interactions observed here are a property of the thin-film geometry, in which the solid is contained within two parallel surfaces. When investigated in a half space, the same dislocation configuration does suffer attractive forces from the surface. The results show that findings derived for dislocations in a half space do not automatically apply to thin films. Instead, the transition to a confined geometry can bring about quantitatively as well as qualitatively new phenomena.

In support of our findings, we give a critical discussion of image force arguments that underlie earlier work on grain rotation, and verify that the present analysis of image forces does satisfy the boundary conditions at the free surfaces.
The results have implications for the kinetics of rotation of nanoparticles on a substrate and for the stability of grain and subgrain boundaries in thin metal films.

References
Roles of the Interfacial ElectroChemoMechanical Potential, and of the Particle Size, in the SPS Process

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The published results on SPS (of zirconia) are critically analyzed in the light of two sets of recent experiments: (i) the influence of an electric field applied with a pair of electrodes as in “flash sintering”, and (ii) the measurement of electrical fields induced by the application of interfacial stress to irconia. These results, taken together, lead to the hypothesis that the pressure applied in SPS generates electric fields within the polycrystal, which promote densification. It is hoped that this hypothesis, even though speculative, would stimulate a lively discussion of fundamental issues in the SPS process.
In situ Transmission Electron Microscopy Characterization of Interfaces under Externally Applied Stress Fields

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The investigation of structure-property relationships for functional nanomaterials and the determination of mechanisms for defect evolution under extreme conditions is an important task for the development of novel materials systems. In situ transmission electron microscopy (TEM) provides access to the atomic structure and composition of defect structures and enables their characterization as a function of externally applied stresses, such as elevated temperatures, electrical fields and currents, etc.

For kinetically constrained thin films, changes in temperature alter the wetting behavior of thin films on substrates. Unbalancing the current equilibrium state of surface and interface energies can lead to interface reactions and/or rupturing and subsequent agglomeration of the film. Cross-sectional characterization of as-deposited nickel films on silicon surfaces and subsequent annealing has revealed complex interface structures and their evolution that strongly depends on the presence of silicon surface oxides [1] as well as possible alloying elements such as Pt [2]. It was found that the presence of ultrathin native oxide films covering the substrate surface prior to film deposition controls the growth of nickel silicide films with gradually changing composition and structure [1]. Subsequent annealing during in situ TEM observation indicates that film agglomeration to minimize the interface energy competes with the formation of stoichiometric NiSi₂, which corresponds to the most stable silicide phase in contact to the single crystalline substrate.

In the absence of a surface oxide film the formation of a “pre-silicide layer” was observed during two-step rapid thermal annealing of Ni/Si interfaces (see figure 1) [2]. The proposed pre-silicide layer arises from a disparity between the propagation of the interstitial diffusion front for Ni in silicon compared to the growth dynamics of Ni₄Si and NiSi under source-limiting conditions. It was found that alloying of the Ni films with 10at% of Pt significantly further alters the growth kinetics for Ni₄Si and NiSi due to Pt segregation to both grain boundaries in the silicide film and the silicide/substrate interface. Aberration-corrected scanning transmission electron microscopy revealed several different point defect configurations for Ni within the pre-silicide layer (figure 2). The observed point defects were found to increase the Schottky barrier height of the rapid thermally annealed Ni(Pt)Si/Si interface structures.

The wetting of metallic surfaces by ultrathin films of their respective oxides plays a critical role for the dynamics of densification during electric field assisted sintering (EFAS). In situ TEM techniques were used to investigate possible “surface cleaning effects” that may control the early stage of densification during EFAS of nano-granular powders. It was found that ultrathin NiO layers that cover nickel nanoparticles with diameters of approximately 20 nm can be removed either by reduction-oxidation reactions at 450°C [3] or by electric field-induced dielectric breakdown (figure 2) [4].

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Figure 1: Annular dark field image of a Pt-alloyed NiSi film deposited on a single crystalline silicon substrate. Two stable interstitial configurations were observed for Ni atoms embedded in the pre-silicide layer (graphical abstract for [2]).

Figure 2: Micrographs of two contacting Ni nanoparticles before (a) and after successive exposure to electrical fields (c & d). Ramping electrical fields were applied through contacting a nanoscale electrode to the particles located on the TEM sample holder. Resulting I-V curves are plotted in (b). Figure reproduced from reference [4].

References
Motion and Shear of Faceted Grain Boundaries

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The migration of grain boundaries has often included the concept that “special” boundaries behave in a manner that is different from high angle grain boundaries. There are several suggested mechanisms for the difference in boundary migration rates for “special” boundaries. These mechanisms span the range from chemical to structural and predict a wide range of behavior. Thus it is difficult to identify what it is about boundaries that make them special. In this presentation we will discuss how the faceting of grain boundaries can be studied independent of other factors and what the effect of this faceting on motion will be.

There have been many studies of the motion of boundaries that have examined the behavior of special boundaries and proposed mechanisms to explain the observations. One is that the structure of a special boundary is significantly different and thus the rate at which defects can be created and annihilate at these boundaries will be lower than a random high angle grain boundary [1,2]. Another mechanism is that boundaries near low energy orientations will facet into structures composed of straight segments composed of low energy facets and random high energy segments [3,4]. A third possibility is that the boundaries undergo structural or wetting transition with slight changes in composition or orientation [5]. All of these mechanisms are likely to be active at the same time resulting in a range of behavior that is dependent on conditions that are not well controlled. This makes the understanding of grain boundary migration in systems that have anisotropic interfacial energies and diffusion controlled by extrinsic dopants very difficult to achieve.

In MgO, studies by Saylor et al [6] have shown that the grain boundaries have a preference for specific orientations related to the surface facets observed. Boundaries tended to have one orientation aligned with a surface facet direction indicating that the Wulff shape of a material can be used to predict that the structure of grain boundaries is likely to be faceted when the free surfaces are faceted. In the NiO-MgO alloy system we have shown that the surface faceting can be controlled by changing the composition [7]. Figure 1 shows the range of faceting that can be achieved. Also, Vaudin et al have shown that grain boundaries in NiO exhibit faceting on the nanoscale as has also been observed in alumina [8,9]. We have also predicted that the grain boundary structures are limited to four general types depending on the orientations of the grain surfaces [10] as shown in Figure 2.

In this presentation we will present a model that relates the faceting of grain boundaries to the migration rate and discuss the possible couplings between applied fields and motion of a grain boundary [11]. Ongoing studies in the model systems MgO-NiO and SrTiO$_3$ will be presented and examples from the alumina-anorthite will also be discussed.
Figure 1: Observe range of facet behavior in MgO-NiO alloys at 1600°C [7].

Figure 2: Possible facet structures for grain boundaries when the Wulff shapes are fully faceted [10].

References
Dynamics at the Growth Interface During the Formation of Semiconductor Nanowires

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The use of catalytic particles to grow semiconductor nanowires, through the vapour-liquid-solid or vapour-solid-solid processes, can enable new and exciting structures to be created. Appropriate choices of reactive gases, catalysts and growth parameters allow us to form nanowires that incorporate compositional gradients to form structures such as quantum wells; we can integrate materials with different lattice parameters, and even grow non-equilibrium crystal structures. This highly controlled growth is advantageous for a range of electronic and energy applications. But it requires a detailed understanding of the mechanisms that control nanowire formation, and the pathway of the atoms through the catalyst and on to the growth interface. In situ observations made during growth can provide useful information towards achieving this aim. We have therefore developed a set of in situ transmission electron microscopy techniques that allow video-rate observation of the structure and dynamics of the growth interface during the formation of semiconductor nanowires [1]. By flowing reactive gases such as disilane, digermane, trimethylgallium and phosphine into the microscope so that they impinge upon a heated sample with catalytic particles, or a sample with pre-grown nanowires such as in Figure 1, we can grow nanowires in situ, imaging the phase and physical dimensions of the catalyst and nanowire and the flow of steps at the growth interface between catalyst and nanowire.

Exploring different catalyst compositions allows analysis of the effect of the catalyst phase, liquid versus solid, on nanowire growth [2]. We find that solid and liquid catalysts display different behaviour in terms of step flow kinetics and compositional gradients at heterojunctions. These differences can be explained by considering the supersaturation of the growth species in the catalyst [3]. Furthermore, the growth interface itself shows a periodic oscillation at the trijunction, the location where catalyst, nanowire and vapour meet (Figure 1b, c). This oscillation is synchronised with the flow of steps at the growth interface, and can be understood by considering the energies of the interface and surface as the supersaturation varies during the step flow cycle [4]. The trijunction oscillation is particularly useful in that it allows us to measure the exact time at which each step flows. We can therefore correlate the local growth rate (the time interval between addition of atomic layers) with the local structure of the nanowire.

During the growth of an individual Si nanowire from a liquid AuSi catalyst, the interval between step flow events is constant, leading to a steady growth rate that depends on pressure, temperature and diameter in the way expected from the vapour-liquid-solid mechanism [1]. However, for GaP growing from liquid AuGa, we find that the growth kinetics are far more complex, even for a single nanowire. The volume of the catalyst, and hence its Ga content, depend on the ratio of group V to group III sources (i.e. the phosphine/trimethylgallium ratio). Under conditions of low group V supply and high group III, as in Figure 1d, the droplet is Ga-rich and the growth rate is steady and depends linearly on the group V pressure. However, under conditions where the group V supply is not the limiting factor, the local growth rate varies within a single nanowire. We find that when a twin plane defect forms in the nanowire, the next several layers grow at a faster rate before returning to the pre-defect rate. This unexpected behaviour can be modeled by considering the chemical potentials of the two species, the phase and composition of the catalytic droplet, and the pathways by which the species arrive at the growth front. We believe that understanding growth
kinetics and catalyst phase at this local level may help in developing more precise control of crystal structure in compound semiconductor nanowires.

Figure 1: GaP nanowires grown from 45nm diameter Au aerosol particles. The horizontal features are twin plane defects in the zinc blende structure. (a) Nanowire imaged after growth showing solid Au at the tip. The wire was formed by metallorganic chemical vapour deposition at 500°C with TMGa = 9.2×10^8 Torr and PH3 = 1.2×10^2 Torr (V/III = 1340) in H2 at 61/min. (b) A similar nanowire imaged during growth of additional GaP (arrowed region) in situ in the TEM at 440°C with TMGa = 5×10^8 Torr and PH3 = 1.0×10^2 Torr (V/III = 200). Growth is from a liquid AuGa catalyst. Since the initial Au volume is known from (a), the droplet size allows an estimation of the AuGa catalyst composition during growth, ~24% Ga, ignoring changes in atomic volume on alloying. (c) The same nanowire 140s later, immediately after flow of a step at the growth interface. Truncated regions are visible at the trijunction (arrows). The scale bar applies to (a), (b) and (c). (d) Growth of a different nanowire at 435°C under Ga-rich conditions, with TMGa = 3.5×10^7 Torr and PH3 = 1.0×10^5 Torr (V/III = 28). The large droplet has a composition of ~75% Ga.

References
Using Dynamically Scattered Electrons for Retrieving 3D Atomic Positions in Nanoparticles

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Nanoparticles, because of their high surface area, corners, and edges per amount of material, i.e. the large number of atoms being located in a non-bulk environment, are at the core of many modern energy and catalysis applications. Exploring the potential that nanomaterials offer for these important fields targeted by the MACAN project requires also techniques to characterize the origin of their very special properties, the 3D arrangement of atoms within them, and in particular the positions of atoms being exposed to their environment. The only technique currently available for measuring the positions of atoms within and on the surface of nanoparticles is transmission electron microscopy (TEM). While TEM experiments are in most cases quite straightforward, the quantitative analysis of the acquired data is still challenging. We have recently developed a computer algorithm which solves two very important problems in the field at once [1]:

a) **The dynamic inversion problem**, i.e. the problem of quantitatively interpreting high-resolution images in terms of the structure of the scattering object: This challenge has fascinated several experts in the field, and many more have identified the dynamic inversion problem as the major unsolved problem in TEM. So far, no convincing and experimentally easily realizable solution has been found. At the same time, with the current trend to work at accelerating voltages as low as 40, 30, or even 20 kV, the importance of being able to invert the multiple elastic scattering of electrons increases dramatically. We show that noisy high-resolution TEM (HRTEM) images (not exit face wave functions, as in our earlier attempts [2]) acquired at different tilts are sufficient to solve the dynamic inversion problem (see Fig. 2). And even the modulation transfer function (MTF) of the camera as well as aberrations and partial spatial and temporal coherence of the microscopy are taken into account.

b) **Efficient atomic resolution tomography**: Conventional, linear tomographic reconstruction algorithms (weighted back-projection, SIRT, ART, etc) and even the recently much celebrated DART algorithm rely on a linear, or at least monotonic mass-thickness/contrast relationship which does not exist in HRTEM images. At atomic resolution such algorithms are therefore applied to tilt series of either high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, negative spherical aberration (NCSI) images, or the phase of reconstructed exit-face wave functions, acquired for a large range of tilt angles of at least $\pm 70^\circ$. Fig. 3 shows that atomic resolution in the direction parallel to the incident electron beam can already be achieved for a tilt range of $\pm 10^\circ$, if electrons have scattered multiple times (see Fig. 1 for a comparison of kinematical and dynamical scattering), a resolution that would be impossible with a linear reconstruction algorithm for such a small tilt range. In addition to the much more quantitatively accurate treatment of the available data by this algorithm, the acquisition of conventional HRTEM data for a small tilt range is much simpler and dramatically reduces the electron dose which the sample is exposed to.
Figure 1: Comparison between a dynamical and a kinematical simulation of a nanoparticles consisting of 309 Au atoms imaged with 40 kV electrons. The particle is imaged at zero tilt (scale bar = 1.5 nm).

Figure 2: Five typical simulated input images, the tilt around the horizontal axis of these images is 0° and around the vertical axis, from left to right, -10°, -5°, 0°, 5°, and 10° (scale bar = 1.5 nm).

Figure 3: Comparison of atomic potential of input model and reconstruction: Upper two rows: Slices with the projected potential of the Au particle; the gray scale is logarithmic. Middle two rows: Reconstructed projected potential (scale bar = 1.5 nm).

References
Mapping Nanofields by Electron Holography

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Transmission Electron Microscopy (TEM) is a tool particularly powerful for the studies at the nanoscale of structures, microstructure (in imaging mode), chemistry and electronic structures (in spectroscopy mode) of (nano)materials. In conventional TEM only the intensity and energy loss distribution of the electronic beam is measured, while information concerning the phase shift of the electron wave is lost. The e-beam phase shift is however sensitive to the electrostatic and magnetic fields the beam has interacted with [1-3] and we recently showed that the phase of the electron wave is also sensitive to strain fields [4]. Measuring the e-beam phase shift should then give access and map all these fields with the spatial resolution of the TEM. Electron holography (EH) is an interferometric method which allows the amplitude and the phase shift of the high energy electron wave to be recorded. I will show that EH is able to quantify and map local electrostatic and magnetic fields (both inside the sample and in the surrounding leakage fields) and strain fields with a resolution of the order of few nanometers on large field of view.

I will first describe the experimental EH procedure allowing the quantitative measurements of magnetic fields in nanostructures and illustrate the potentialities of this method studying the magnetic configurations in magnetic nanomaterials.

In a second part, I will present the new “Dark-field Electron Holography” method [4], which permits to measure strain field in crystalline materials with an accuracy of about 0.02% and a spatial resolution of 2 nm over regions larger than 2 microns. Examples on strained Si - MOSFET and Si Fin-FET transistors will be presented to illustrate the capability of the method [5].

In a last part I will show how EH allows to measure elemental charges in nanostructures.

References
Toward Atomic-Scale Tomography

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Atom probe tomography (APT) is a three-dimensional atomic imaging technique. Yet it fails to reach the ultimate in microscopy which is seeing every atom with high precision in large volumes. This talk will review the state of the art in APT and explore what it would take to reach the next level which is defined to be atomic-scale tomography (AST). The potential impact of AST on science and technology will be considered.

Figure 1: APT image of the functional components of a commercial white LED device.

‘Off the Shelf’ APT analysis of a white LED

GaN
In
Al
Mg
50 nm

Indium Super-lattice

Indium Quantum Wells
The Growth of Alumina Scales on High Temperature Structural Alloys


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Ni-based and Fe-based structural alloys exposed to the highest operating temperatures in oxidizing ambient depend on the formation of a passivating Al2O3 scale for the requisite oxidation resistance. Most investigators have attempted to interpret Al2O3 scale formation in terms of Wagner’s classic theory of oxidation, which has proven very satisfactory for transition metal oxides such as NiO and CoO. Different from Al2O3, the electronic conductivity, σe, for these materials is much greater than the ionic conductivity, σi. For Al2O3, the transference number (σi/σi+σe) is of order 0.5, and there is thus need to pay attention to the electrical properties of Al2O3 scales. Further scale formation occurs primarily by grain boundary as opposed to lattice diffusion, again not the case for NiO and CoO.

Finally, it has been known for many years that small alloying additions (<1 wt %) of the so-called “Reactive Elements” (REs) – particularly Y, Hf, and Zr – improve oxidation resistance by i) increasing the adherence of the scales to the structural alloy and ii) decreasing the oxidation kinetics. Explanations of their effectiveness have been qualitative and generally lacking in rigor. Recently [1] it was suggested that the REs, which segregate to scale grain boundaries, affect scale formation by modifying the electronic (band) structure, in particular the near-band-edge defect states contributed by grain boundaries.

In this two part presentation, we review recent experimental and theoretical progress relevant to Al2O3 scale growth. The theoretical models of point defects and their possible role in diffusion and high temperature corrosion have provided new insight into this important aspect of high temperature technology.

Our calculations of the structure and energetics of point defects in bulk Al2O3 with density functional theory (DFT) revealed several new features [2]. To begin with, the role of the chemical potential of the electrons (loosely referred to as the Fermi energy εF) is crucial, since, as shown in Fig 1, it makes an important contribution to the formation energy of charged defects such as V′′

v

, V′

v

, Vm

αι

 and Vn

αι

 (Kröger–Vink notation), as its magnitude determines their equilibrium concentrations and which defect is dominant. Through the thickness of a scale, according to Wagner theory, an electric field is set up that could shift εF through the scale sufficiently to change the dominant equilibrium defects from aluminum vacancies at the oxide-gas interface to oxygen vacancies at the oxide-metal interface. Thus within the thickness of a scale, the mechanism of ionic conduction and its magnitude is likely to change drastically. While we know little about the electrical conductivity, except that there has to be some in order to balance the electric current carried by diffusing ions, we also expect the charged defects to supply the electron or hole carriers.
These concepts will translate to the defects that mediate grain boundary transport. Although we still know little about the possible structures of the defects, we can be confident that they will be more varied than the bulk defects. An important aspect in the electrical conductivity will be played by the density of states at the band edges, and our calculations show how this is strongly altered at a grain boundary, which is where we expect most of the conduction of all species to take place.

Preliminary results for defect structures and formation energies in grain boundaries are reported, in which new interatomic potentials of the Tangney-Scandolo type [3] are used for obtaining plausible boundary structures, which are studied in detail with DFT.

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Figure 1: Formation energy of the charged vacancies in Al₂O₃ as a function of the chemical potential of electrons, measured from the top of the valence band.

References
Pt Precipitates in Polycrystalline Alumina—
A Model System for Investigation of Metal Equilibration in Ceramics

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The investigation of metal-ceramic materials has significance both in fundamental science and in many technological applications. Transient and equilibrium shapes of metals in ceramics affect the mechanical, optical, and electronic properties, and the long-time thermal and mechanical stability of the metal-ceramic composites. Nevertheless the transient and equilibrium shapes in metal-ceramic composites are not yet fully understood.

In the current talk a model system of Pt particles embedded in polycrystalline α-alumina will be presented. This system is used to explore and define the path and rate of evolution of nanoscale metal particles embedded in ceramic media, and specifically the role that the crystallographic orientation relationship (OR) and interfacial structure between the Pt and alumina have on affecting the ultimate equilibrium shape and the kinetics of evolution towards that equilibrium shape.

The experimental system is created by implantation of polycrystalline alumina with Pt ions [1]. The implanted specimens were annealed at 1565°C for 5, 25, and 100 hours in order to reveal various stages of the Pt ripening and equilibration. Grain-growth of the polycrystalline alumina, which occurred in parallel with Pt equilibration, can induce a change in the Pt-alumina OR, and thus provides an experimental vehicle for investigating the kinetics of Pt particle shape (re-)equilibration in response to and as a function of the newly imposed OR.

An example of alumina grain-growth can be seen in Figure 1. The smaller alumina grain (Figure 1.b) is being consumed by the larger surrounding grains. The Pt particles occluded in the growing alumina grains, adjust their shape in response to the new OR. Additional stages of the Pt re-equilibration were investigated in specimens annealed for 25 and 100 hours. In addition to the studies of equilibration kinetics, the presented system is also used to investigate equilibrium Pt shapes in alumina. Previously the full shape equilibration could not be achieved due to the pinning of Pt/alumina interfaces that were parallel to the low-energy (0006) plane of the sapphire [2]. However, in the current set of experiments, the consumption of Pt particles by the growing alumina grains moves the Pt out of equilibrium with alumina, disrupts the existing facets, and may lead to full equilibration of the particles in the new alumina grain. An example of fully equilibrated Pt particles is presented in Figure 2.
Figure 1: Plan-view BF-STEM micrograph of (a) Pt-implanted polycrystalline alumina annealed for 5 hours, and (b) a magnified view of the circled region in (a).

Figure 2: Sample annealed for 100 hours: (a) HAADF-STEM micrograph of Pt-implanted alumina, and (b) Cs-corrected (Cs=−5.5μm) HR-TEM micrograph of a Pt particle marked on (a).

References
Synthesis of Advanced Metal-Ceramic Composites via Controlled Interface Reactions

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Liquid-reaction processing of ceramic composites represents a fast and simple manufacturing route to high-performance components exhibiting the potential for low cost synthesis of complex structured components. For example, the infiltration of Al based melts into reactive porous precursors can be performed using conventional casting techniques and - due to an in-situ synthesis of the desired product phases – refractory products can be formed offering application temperatures close to the synthesis temperature. Two examples will be the focus here: Alumina-Aluminide Alloys (3A) and Alumina-reinforced FeNiCr alloys. For both variants, the reactions at the interface play an essential role. For 3A materials, these reactions favour the overall synthesis progress due to their exothermic nature. In contrast, the formation of transient diffusion barriers is the essential “trick” for the reactive synthesis of high performance FeNiCr composites. In the presentation, the recent understanding will be outlined with special emphasis to the resultant process window.
Correlation between Structure of Interfaces and Active Sites and Aging Properties of Noble Metal Catalyst Particles on Oxide Supports

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Noble metal particles are used for the abatement of the toxic gases NO and NO₂ (NOₓ) from car exhausts of diesel or lean-burn gasoline engines. These engines have better fuel economy and are therefore preferred considering that the consumption of fossil fuels needs to be reduced due to economical and environmental aspects. However, the existing standard three-way catalysts cannot reduce the NOₓ species that are formed. They are harmful and are, for example, responsible for acid rain, forming ground-level ozone (which in turn is the major constituent of smog) and are also increasing the risk of respiratory allergies. It is therefore important to remove the NOₓ species by exhaust gas after-treatment. During use, the efficiency of the catalysts is degraded where the mechanism responsible for the degradation can be either of thermal or chemical nature. Crucial aspects of the performance of the catalysts are the active sites and also ageing properties.

The interface between the noble metal particles and the oxide supports in catalysts controls both the size and morphology of the particles, see Fig. 1, and is thereby also affecting the active sites. This talk will address the effect of the interface between noble metal particles and oxide supports on the efficiency of the catalysts and on the ageing properties, see Fig. 2, in different gas compositions. The activity, ageing and dispersion measurements are carried out in bench reactors. The mechanisms of degradation and the structure of the particles and interfaces are studied using electron microscopy and in particular high resolution transmission electron microscopy (TEM) and scanning TEM (STEM). High angle annular dark field (HAADF) STEM imaging using a probe corrected Titan TEM instrument provides Z-contrast information revealing the distribution of the noble metals on the oxide support with atomic resolution. Complementary information is extracted using monochromated electron energy loss spectroscopy (EELS) in the Titan TEM and x-ray diffractometry (including measurements at the European Synchrotron Radiation Facility).
Figure 1: STEM HAADF images of Pt particles on a) SiO₂ support and b) Al₂O₃ support. The samples were fabricated using identical parameters and the difference in Pt particle size is due to the difference in interaction at the interface between the particles and support.

Figure 2: STEM HAADF images of Pt particles on Al₂O₃ support. a) As received sample. b) Aged in 10% O₂ and 30 ppm SO₂ at 900 °C for 2 h.
Stress Relaxation in Tin Thin Films: From Whiskers to Grain Growth

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Whiskers and hillocks have been observed to grow spontaneously from Sn thin films in response to in-plane stresses. Stress relaxation occurs by diffusion to specific grain boundaries in the plane of the film, leading to an out-of-plane relaxation, with hillocks being formed when grain boundary migration accompanies growth out of the plane of the film. The implication of whisker formation in electronics is serious: whiskers in Sn films can grow to be millimeters long, sometimes causing short circuiting between adjacent components and, thereby, posing serious reliability risks. In order to understand from a scientific point of view as well as to develop more effective whisker mitigation strategies for electronics, a predictive physics-based model has long been needed. In this presentation we introduce such a physics-based model for whisker and hillock formation in thin films as well as experimental evidence of the local dynamics of stress relaxation as the stress state changes. In particular, hysteretic phenomena observed in-situ during thermal cycling reveal the changing state of the film and its ability to relax stresses at the gain level.

Our model is based on the coupling between localized Coble creep and grain boundary sliding in stressed thin films and includes the effects of grain geometry and size and grain boundary properties on the growth of whiskers and hillocks. For both whiskers and hillocks, accretion of atoms by Coble creep on grain boundary planes normal to the growth direction is limited by grain boundary sliding on planes parallel to the direction of whisker growth. If the accretion-induced shear stresses are not coupled to grain boundary migration a whisker forms when sliding occurs, as shown schematically in Figure 1. In the case of hillocks an additional coupling between grain boundary sliding and shear-induced grain boundary migration leads to the observed lateral growth. By incorporating grain size and geometry, a structure-dependent grain boundary sliding coefficient and measured film stresses the local conditions for whisker growth, including the growth rates, can be calculated. The model accurately captures the importance of the geometry of "surface grains" - shallow grains on film surfaces whose depths are significantly less than their in-plane grain sizes. A critical factor in the growth analysis is the ratio of the grain boundary sliding coefficient to the in-plane film compressive stress. Based on this model, long whiskers grow from shallow surface grains with easy grain boundary sliding in the direction of growth. Specific growth morphologies observed from Sn, Ag, and Au films will be discussed in light of our model.

In-situ observations of Sn thin films on W or Cu/Si substrates during heating and cooling at CINaM and NIST have revealed widespread microstructural evolution and surface defect formation that are not obvious from ex-situ examination of films before and after thermal cycling. Whisker and hillock formation, grain rotation, fatigue crack formation and grooving fracture of surface oxides, grain retraction, hole formation, whisker pinch-off, and the effect of surface oxide layers on the relaxation hysteresis during heating and cooling all provide evidence for local stress relaxation that take various forms.
Additional insights into the preferred sites for whisker and hillock growth in Sn films have been developed based on ex-situ measurements and modeling of elastic anisotropy, local film microstructure, grain misorientation, and elastic strain energy density (ESED) as the driving force for growth. Based on the models and experiments presented here, a clearer picture emerges of the necessary and sufficient conditions for whisker and hillock formation in thin films.

Figure 1: (left) Classic Sn whisker (right) Schematic of a simple surface defects growth model, delineating the roles of atomic accretion, faceting of the grain boundary (facets shown by blue vertical line and red horizontal double lines), and grain boundary sliding (along the sliding planes shown by blue vertical lines) on surface defects formation from a surface grain with ($0^\circ<\theta<90^\circ$).

Figure 2: Hole fill by surface diffusion during heating in ultra-high vacuum SEM hot stage experiments on Sn films on W substrates (time sequence, increasing temperature and time during heating, left to right).

References
Interface Thermodynamics under Mechanical Stresses: Theory and Atomistic Modeling

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Thermodynamic properties of interfaces have been traditionally described in terms of the Gibbs absorption equation which was originally derived for fluid-fluid interfaces [1]. In this talk we present some of the recent extensions of the Gibbsian thermodynamics to solid-liquid and solid-solid interfaces when the solid phase(s) is/are subject to non-hydrostatic stresses [3-6]. We also discuss some of the applications of the new thermodynamic treatment to atomistic simulations.

Solid-liquid interfaces in multicomponent systems under mechanical stresses. A generalized adsorption equation has been derived with additional terms representing the work of the lateral components of the non-hydrostatic stress tensor $\sigma_{ij}$ inside the solid [3,4]. The differential coefficients of this equation are interface excesses of extensive properties, which we treat using Cahn’s [2] formalism. In this formalism, the excesses are defined without using a dividing surface or the need to compute density profiles across the interface. The generalized adsorption equation leads to the formulation of the interface stress $\tau_{ij}$ as an appropriate excess over $\sigma_{ij}$. We show that $\tau_{ij}$ is not unique unless the solid is in a hydrostatic state of stress. We also derive Gibbs–Helmholtz forms of adsorption equation which can be applied for thermodynamic integration to compute the interface free energy $\gamma$. The proposed thermodynamic integration methods offers a remarkable flexibility in choosing the integration path via the selection of different types of interface excesses.

As an application, we present the recent semi-grand canonical Monte Carlo simulations of solid-liquid interfaces in copper and Cu–Ag alloys [3-5]. The interface free energy computed by thermodynamic integration along the phase coexistence path increases with temperature (Fig 1). Both components of $\tau_{ij}$ are negative, i.e. the solid-liquid interface is in a state of compression. As temperature decreases, the components of $\tau_{ij}$ drastically increases in magnitude and become highly anisotropic. Other applications of this thermodynamic theory to atomistic simulations will also be discussed.

Coherent solid-solid interfaces under mechanical stresses. Fully coherent solid-solid interfaces are capable of supporting shear stresses applied parallel to the interface plane. They respond to such stresses by local elastic deformation. This must lead to additional terms in the adsorption equation with differential coefficients representing the “excess interfaces shears”. We developed a thermodynamic formalism incorporating the shear effect in the adsorption equation and other basic equations of interface thermodynamics [6]. The generalized absorption equation, along with its Gibbs-Helmholtz form convenient for thermodynamic integration, are applicable to any coherent multi-component interfaces subject to non-hydrostatic stresses. The interface stress tensor emerges naturally from the generalized adsorption equation as an appropriate excess over the bulk stresses. The interface excess shear also emerges from our equations as the variable conjugate to the shear stress. As above, all interface excesses are treated without using a dividing surface.
The theory has been applied to atomistic simulations of a symmetrical tilt grain boundary in Cu and Cu-Ag alloys under applied tensile, compressive and shear stresses [6]. We have studied the effect of such stresses on the grain boundary free energy, interface stress, solute segregation, free volume, excess shear and other properties. Using a combination of molecular dynamics and Monte Carlo methods, we computed a number of grain boundary excess quantities as functions of the applied stresses, temperature and chemical composition in the grains. We also tested several Maxwell relations and obtained excellent agreement between the theory and simulations.

As another application, thermodynamic properties of coherent $\gamma/\gamma'$ interfaces in the Ni-Al system have been studied over a wide range of temperatures and applied stresses. These interfaces present a major challenge to simulations (as well as experiments) due to their small free energy, typically on the order of 10 mJ/m$^2$. We demonstrate that the proposed thermodynamic theory and the thermodynamic integration methods permit reliable atomistic calculations of the free energy, interface stress, excess volume, segregation and other properties of the $\gamma/\gamma'$ interfaces. This new capability can be of significant interest to the developers of Ni-based superalloys and can be later transferred to other low-energy interfaces in different materials.

References
Measuring Fracture Toughness Gradients in Pt-Ni-Al Bond Coats with Micron Scale Spatial Resolution

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Diffusion coatings of Pt-Ni-Al that protect superalloys from oxidation in gas turbines are non-equilibrium structures that are graded in composition over ~ 100 microns and evolve in time owing to oxidation-induced loss of Al at the surface and to interdiffusion with a Ni-rich substrate on the blade side. Damage of such coatings occurs due to thermo-mechanical loading and impact damage. Thus, mechanical properties such as fracture toughness and flow stress need to be measured over the ~ 100 micron length scale over which the coating changes from a beta-(Pt,Ni)Al rich surface zone to a mixed beta-gamma prime interdiffusion region near the interface with the substrate.

This talk will first describe a new notched beam bending geometry that allows crack propagation to be studied in different zones of the bond coat. Somewhat unusually, this loading geometry displays stability even under load control. FIBed beams that are rigidly clamped at both ends are notched and subject to ex-situ as well as in-situ testing using a depth-sensitive indentation loading system. Extended FEM analysis is first used to determine stress intensity factors following experimental validation from the compliance. Initiation toughness, measured as a function of Pt content and of position in the coating, is shown to vary from ~ 5 to over 15 MPa m¹/². Crack resistance curves can also be determined over ~ 10 microns while preliminary tests on cyclic loading indicate that fatigue crack propagation can also be studied.

Preliminary high temperature tests on single-edged notched tensile samples will also be described and their results compared with microbeam tests.
Measurement of Grain Boundary Toughness in Ceramics using Microcantilevers

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The toughness of grain boundaries in ceramics can be very influential on the toughness, strength and wear resistance of the bulk polycrystalline material and is an essential piece of information for physically based modelling of any process involving fracture of the ceramic. The grain boundary toughness is known to be influenced greatly by the structure and composition of the boundary but is difficult to measure directly. This presentation concerns attempts to measure the toughness of individual grain boundaries in aluminium oxide ceramics by testing notched microcantilevers with dimensions on the scale of the microstructure using a nanoindenter. The microcantilevers are milled from the ceramic surface using Focused Ion Beams. The validity of the technique is first demonstrated by measurements of the Young’s modulus of single crystals and polycrystals. After a brief discussion of strength results from un-notched beams, attempts to measure the toughness are described, initially of single crystals, then of boundaries in bicrystals and finally of individual boundaries in polycrystals. The influence of notch shape and sharpness and environmentally assisted subcritical crack growth are discussed. The effectiveness of the technique in discriminating between different grain boundaries is demonstrated by a comparison of grain boundary toughness measurements in undoped alumina and carbon-doped alumina.
Toward Computational Design of Wear Resistant Materials: Molecular Understanding of Friction

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It has been estimated that about one third of energy produced in industrialized countries is lost to overcoming friction. Significant reduction in this loss can be made through design of coating materials with superior tribological properties for use in transportation and industrial production. Although knowledge of fundamental mechanisms underlying friction can enable rational and systematic design of coatings, such an approach has been hindered by the limited understanding of basic physical and chemical processes taking place in the sliding contact. The basic laws of friction were first proposed by Leonardo da Vinci in 1699. However, even centuries after this discovery it is still not possible to quantitatively predict friction parameters, such as friction coefficient and interfacial shear strength. The challenges in understanding friction stem from the complexity of energy dissipation mechanisms involved in sliding, which include elastic instabilities, phonon and electronic dissipation, dislocation motion, chemical reactions at the interface, and others.

A transformation of the field of tribology has been recently ignited by the convergence of length scales accessible to experimental studies and to fully atomistic simulations of contact mechanics. In this talk I will discuss specific examples of insights into nanoscale tribology gained from my work using large-scale molecular dynamics simulations with highly realistic empirical potentials combined with ab initio modeling. One example is the discovery of mechanisms that underlie aging of silica in aqueous environments, which is of interest for multiple phenomena ranging from wafer bonding to shallow tectonic earthquakes. We have demonstrated that in the absence of deformation creep, aging of silica takes place by formation of interfacial siloxane bridges. We have discovered a new mechanism for interaction between these bridges and have shown that this interaction is critical to explain experimentally observed logarithmic dependence of aging on time. I will also discuss contributions from my group to understanding of deformation and wear of nanocrystalline materials. For instance, we discovered deformation mechanisms in ultranocrystalline diamond and explained the effects of H dopants on mechanical properties of this material. We have shown that in the absence of dislocation plasticity, yield stress and hardness of nanocrystalline materials scale with grain boundary shear strength.
MACAN Young Scientist Abstracts

Oral Presentations
Electron Microscopy Study of Twinning and Formation of Modulated Structures in Be-Doped MgAl$_2$O$_4$ Spinel

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Twinning in spinel is an interesting phenomenon from the material's structural and morphological point of view. Because of their distinct appearance, (111) twins in spinel as well as in many other cubic minerals, such as magnetite, galena, sphalerite, diamond, noble metals (Au, Pt, Cu), etc. have been termed – Spinel Law twins. Common for these twins is that they are much larger compared to normal, untwinned crystals, grown under same conditions. While crystallographically, the twin operation is a 180° rotation about [111]-axis, with (111)-plane as the interface, there is virtually no knowledge about their atomic structure and chemistry, and moreover, what triggers their formation.

Our challenge, thereby, was to investigate the local structure and origin of twinning in the type mineral, MgAl$_2$O$_4$ spinel. Recent study of (111) twins in spinel crystals from Burma indicated that the twin boundary might comprise one atomic layer of Be residing at the interfacial tetrahedral sites, replacing Mg, however the experimental evidences were not conclusive, because the amount of Be, if present, was too low to detect by any available analytical method at the time of the study [1]. An important clue for the possible origin of twinning was found in the study by Tabatha & Ishii, who grew spinel crystals in flux by the addition of minute quantities of BeAl$_2$O$_4$ (chrysoberyl) [2]. The result was a surprisingly high density of (111) twins in the product. Another indication that twinning in spinel might indeed be triggered by beryllium, is the existence of polytypic phases in the MgAl$_2$O$_4$–BeAl$_2$O$_4$ system with a general formula Be$_x$Mg$_{3-2x}$Al$_{2(x+y)}$O$_{4(x+y)}$. To verify if Be indeed triggers twinning in spinel, and to synthesize the intermediate polytypic phases, we mixed MgO, A$_3$O$_3$ and BeO in different molar ratios and sintered the pellets at 1200°C for 2 hours. PbF$_2$ was used as liquid forming agent in order to accelerate the diffusion processes. We demonstrated that the addition of BeO does not only cause an abundant {111} twinning of spinel, but also complex epitaxial overgrowths of taaffeite-type structures with the following relation to spinel: [110]$_0$ {111}$_{sp} || [1120]_{st} \{0001\}_{taf}$.

Structural analysis of HRTEM images reveals that both, twin boundaries and Be-rich layers in taaffeite, have a characteristic hcp local stacking within otherwise ccp oxygen sublattice. Unique for hcp layers is presence of Be$^{2+}$ in the interfacial tetrahedral sites, whereas the tetrahedral sites in ccp domains are occupied by Mg$^{2+}$. Similar structural elements are found in spinel (ccp) and chrysoberyl (hcp), implying that the intermediate taaffeite-type compounds are manifestation of a structural modulation between the two end phases, whereas twinning in spinel, where the presence of interfacial Be has been indicated, is a preparatory stage of polytype formation [3]. We demonstrated that twinning in spinel is not a consequence of accidental attachment of crystals in nucleation stage, but is chemically triggered through the formation of Be-rich interfacial layer.
Figure 1: Be-induced twinning and formation of modulated structures in MgAl₂O₄ spinel: (a) undoped spinel with simple octahedral crystals and no twins; (b) addition of BeO causes twinning and AGG; (c) by further addition of BeO polytypic taaffeite grows epitaxially of {111} spinel faces; (d) multiply twinned spinel grain with corresponding (e) SAED pattern and (f) HRTEM image; (g) Be-rich (111) twin model (h) spinel-taaffeite interface with the corresponding (i) [110]; {111}sp ||[1120]; {0001}TAF interface model.

References


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Toroidal Plasmonic Eigenmodes in Oligomer Nanocavities for the Visible

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Miniaturization has become one of the pillars of modern technology due to the trend of the electronic devices’ diminishing down to the nanoscale since the beginning of the last decade. Using light for information technology in such devices is impeded by the diffraction limit of light. Converting light into surface plasmons could be a way to circumvent this limit because plasmons have much smaller wavelengths. Therefore plasmonics has become an astonishingly expanding field of technology, which offers numerous possibilities for applications beyond the diffraction limit of light.

Many plasmonic applications are based on electric-dipole and higher-order multipole resonances, as well as magnetic resonances. Here, by energy-filtering transmission electron microscopy (EFTEM) supported with 3D finite-difference time domain (3D-FDTD) simulations we detect the signatures of toroidal resonances in oligomer nanocavities at optical wavelengths, which could not be captured by conventional optical microscopy techniques due to their nearly radiation-free nature. Figure 1 displays a schematic illustration of a toroidal moment. A toroidal moment is composed of combination of electrical and magnetic field loops revolving in radial and azimuthal directions, respectively.¹

Figure 2 illustrates the power of an electron beam to excite various plasmonic eigenmodes, normally requiring different optical excitation setups, all at once. Figure 2a, 2b, and 2c display the acquired EFTEM images, corresponding peak maps, and the results of 3D-FDTD simulations, respectively. Modes II and III reveal the modes having magnetic and electrical dipolar character, accordingly, whereas Modes I and IV correspond to toroidal modes. Even if the central hole is removed, evidence of toroidal behaviour persists, which would be totally impossible to capture with an optical microscopy technique [1].

We believe that toroidal moments have a big potential for novel innovations in the future, such as Purcell effect engineering [2] and data storage and processing [3].
Figure 1: Illustration of a toroidal moment in a plasmonic nanocavity system formed by electric (red) and magnetic field (blue) whirling in radial and azimuthal direction, respectively.

Figure 2: (a) Collection of modes acquired in EFTEM experiment at energy losses of (i) 2.4, (ii) 2.8, (iii) 3.4, and (iv) 3.6 eV. The color code indicates the energy-loss probability in EFTEM images increasing from blue to yellow. (b) Peak maps obtained from the acquired images in (a). (c) Simulated modes with FDTD. Displayed is the modulus of the electric field (|Ez|), color coded increasing from blue to red, at (i) 2.5 eV, (ii) 3 eV, (iii) 3.5 eV, and (iv) 3.7 eV. The scale bar applies to all images.

References
Multiscale Simulations of Grains and Grain Boundaries in Silicon Nitride

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The mechanical and thermodynamic properties of ceramic materials depend strongly on their polycrystalline microstructure. As a consequence, it is possible to optimize the performance of ceramic materials for industrial heavy-duty purposes, such as rolling of sheet metals or bearings in wind turbines, by varying the grain structure and the composition of intergranular films. In practice however the problem of designing a ceramic material based on tailoring its microstructure is still a very complex challenge.

Within the project RoLiCer founded by the European Commission a multiscale simulation approach is being developed with the focus of a better understanding of the effect of the microstructure of Silicon-Nitride-based ceramics. The goal is to identify and formulate knowledge-based criteria which are helpful to the design of novel ceramic materials with improved mechanical performance.

We present a multi-scale modeling ansatz which combines density-functional-theory (DFT) and molecular dynamics simulations, taking into account the properties of model interface systems at the atomic level. We discuss in particular the mechanical and thermodynamic properties controlled by the microstructure and their connection to meso- and macro-scale behaviors.

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Modeling Grain Boundaries in Al₂O₃ Based on DFT

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The formation of a passivating Al₂O₃ layer on the surface of components made of aluminum-containing Fe- and Ni-based alloys protects them from corrosion in oxidizing environments when applied, for instance in turbine blades or furnaces. As the quality of protection is determined by the growth rate of the scales, transport of mass and charge along Al₂O₃ grain boundaries has been a subject of many experimental investigations [1]. In particular, the slowing down of the transport and therefore the oxidation rate due to doping with yttrium is certainly one of the most interesting and important phenomena which we aim to address in the long term from a first principles based modeling perspective.

As it is not clear to what extent the mass and charge transport properties along experimentally relevant grain boundaries is controlled by their electronic density of states, finding their relevant ground state structures is a prerequisite for any further in-depth analysis. Clearly, tackling this problem directly using first principles methods is hopeless as the configuration space for these grain boundaries is vast. Therefore, in the first part of our presentation, we will introduce an empirical force field model fitted to DFT calculations and capturing very well the ground state properties for all stoichiometries in the entire Al₂O₃-Y₃O₃ system. Adding to this, we find also a very good agreement to experimentally measured thermodynamic quantities such as the heat capacity and the thermal expansion coefficient for a selection of materials even at temperatures greater than 1000 K, rendering this potential an excellent tool for studying Y doped Al₂O₃.

With the help of this force field we devised a simulated annealing procedure especially tailored to systematically finding plausible candidates for ground state structures of experimentally relevant grain boundaries. As a first example, we applied this to the symmetric tilt boundaries Σ7(4510)[0001], Σ7(2310)[0001], Σ21(4510)[0001] and Σ21(2310)[0001], whose structural as well as oxygen transport properties have been studied experimentally by Ikuhara et al. [2, 3].

The simulated annealing produces for the Σ7(4510)[0001] and Σ21(4510)[0001] boundaries a distinct atomic arrangement that can be most easily understood in terms of highly ordered, meandering columns of four- and fivefold coordinated Al atoms, giving rise to a prominent fingerprint peak in the electronic band structure above the valence band maximum (see Figure 1).

In contrast, the Σ7(2310)[0001] shows a whole range of structurally different, yet energetically similar atomic configurations. This supports the notion that this type of boundary might have a tendency to display a certain degree of disorder. As the oxygen mobility in this type of boundary is experimentally found to be significantly larger compared to the Σ7(4510)[0001], we will end our presentation with a brief discussion of the implications of our findings for the transport mechanism of oxygen in these grain boundaries.
Figure 1: Electronic density of states of the $\Sigma(4510)[0001]$ grain boundary. The two topmost panels show the projection onto the oxygen and aluminum atoms in the grain boundary core region, whereas the two lower panels show same projection on the indicated species from within the bulk-like region in the center of the grains.

References
Crystal Growth Dynamics of III-V Nanowires via the VLS Mechanism

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Understanding and controlling the dynamics of nanowire (NW) growth are of great practical importance. This is because the NW electronic and optoelectronic properties depend ultimately on the shape and size of the growth interface region during growth. I will in this talk discuss a newly proposed theoretical framework [1] which can be used to analyze the complicated mechanisms of III-V nanowire growth, in terms of the basic control parameters; substrate temperature (see figure 1) and beam fluxes/vapor pressures.

Detailed growth simulations of GaAs (Figure 1) and InAs (Figure 2) [2] nanowire growth will be discussed and compared with experiments. The theoretical framework is based on a continuum formalism where the consideration and quantitative description of all the relevant dynamic processes, such as mass transfer, nucleation limited growth and dynamical reshaping of interfaces is taken into account. The modeling consists of many time-dependent and numerically solved coupled equations involving the material and growth parameters.

The VLS system consists of a solid crystal which is partially wetted by a droplet which at the same time is changing in size during growth. For a full description of the growth region a complete set of independent parameters is needed. That is, we allow for the fact that adding matter to a nanosize crystal will change not only its volume, but also its shape, and therefore the interface excesses. In addition to its volume, the crystal must thus be defined by a set of parameters \{X\} such as facet areas, projected facet heights, facet angles and edge lengths.

While we match the theoretical predictions directly with the III-As NW growth experiments, we stress that the theoretical formalism will be useful for other NW material systems as well.
Figure 1: The substrate temperature has a strong influence on the evolution of Ga assisted GaAs NW growth. Here an investigation of the upper growth temperature limits. The two growths are grown under exactly same conditions, but with two different temperatures that were measured just before initiation of the growth with a pyrometer as $T_{\text{pyro}} = 630^\circ\text{C}$ and $T_{\text{pyro}} = 630^\circ\text{C}$. The activation enthalpy for the adatom to vapor transition of Ga adatoms on the oxide is set to half the value of the modeling on native oxide and the As species was set to desorb immediately from the oxide. In the simulations (shown on the right) the sharp temperature transition occurred at $T_{\text{simulation}} = 661^\circ\text{C}$ and $T_{\text{simulation}} = 667^\circ\text{C}$, which just means that there is still some fine tuning of parameters left to be done.

Figure 2: SEM images of Au assisted InAs nanowire growths where the competition of In atoms plays a key role on the nanowire growth rate.

References
Transmission Electron Microscopy Insights into Photo-Electrochemical Water Splitting-Active Hematite Nanostructures

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The last few years have seen a surge of research in fields related to renewable energy. Solar energy in particular is a promising contender as it is a nearly endless resource which could easily power all of the earth’s energy needs [1]. However, storage of solar power to compensate for night, cloudy conditions and so forth is a challenge. Of the many possible storage options, the conversion of solar energy into chemical energy via the splitting of water into hydrogen and oxygen offers an elegant and practical approach. The resulting hydrogen can easily be stored, transported and used in a fuel cell to regain electrochemical energy.

A material suited for this task should have a small semiconductor band gap to allow for sufficient light absorption, conduction and valence bands spanning from the oxygen oxidation to the hydrogen reduction potential, a high conversion efficiency and be stable in water, all while being cheap enough to allow for mass production [2]. All of these requirements are difficult to meet with one material alone, leading to the creation of electrochemical cells in which the band gap requirements are fulfilled by a photoanode performing the oxygen evolution reaction while the hydrogen evolution takes place at the cathode. Of these two reactions, our work is focused on materials catalyzing the light-driven oxygen evolution reaction (LOER) which, at the moment, is the performance-limiting factor [3].

Hematite, in particular, is a very promising photoanode candidate for a multitude of reasons [4]. It is abundant and therefore cheap as well as non-toxic and consequently easy to handle. Hematite absorbs in the visible region of the solar spectrum and a maximum efficiency for the conversion of solar energy to hydrogen of 16.8 % has been predicted [5].

Our research has so far been focused on mesoporous, Sn-enriched Fe₂O₃ thin films. A mesoporous structure allows for strong light absorption, which could also be reached using thick, flat layers. However, the latter would also lead to large recombination losses in the bulk which are prevented by meso-porosity. The incorporation of Sn was found to increase the efficiency of hole transfer to the OER, leading to a significant increase in photocurrent [6]. In addition, ultra small Co₃O₄ particles were applied as a surface treatment, leading to a significant increase in photocurrent by reducing recombination.

The morphology and chemical composition of these samples was analyzed using Transmission Electron Microscopy (TEM) and related methods such as Electron Energy Loss Spectroscopy (EELS) and Energy-Dispersive X-Ray Spectroscopy (EDX). In my talk, I will give a summary of these results as well as of unresolved issues. I will then detail future experiments with which I intend to answer these open questions. Of interest are, for example, the intermediate species at the surface of the hematite nanoparticles as well as the interface between hematite and the transparent conducting oxide substrate.
References

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Thin films of hydrogenated amorphous Si (a-Si:H) are used as active absorber layers in solar cells deposited on steel foil by roll-to-roll processing [1]. In order to improve the efficiency of such solar cells, the nature of the defects that act as charge recombination centres and decrease the internal electric field in the active Si layer needs to be understood. We have used electron energy-loss spectroscopy (EELS) in the transmission electron microscope (TEM) to study n-i-p thin film Si solar cells grown on steel foil or glass substrates. For a solar cell in which an intrinsic a-Si:H layer is sandwiched between 10-nm-thick n-doped and p-doped a-Si:H layers, we assess whether core-loss EELS can be used to measure the diffusion of B from the p to the i layer. The difficulty of such measurements results in part from the fact that the energy-loss near-edge structure from the Si L edge interferes with the B K edge at 188 eV. In addition, the Si L2,3 edge cross-section is five times larger than that of the B K edge. We use dedicated EEL spectrum acquisition and fitting procedures to reduce the detector noise and to separate the B K edge contribution from the Si fine structure for B concentrations as low as 1 at. %. We compare the shape of the measured B K edge with real space ab initio multiple scattering calculations and show that it is possible to separate the weak B K edge peak from the much stronger Si L edge fine structure by using log-normal fitting functions. We also assess whether changes in volume plasmon energy can be related to the electrically active B concentration and/or to the density of the material and whether variations of the volume plasmon line-width can be correlated with differences in the scattering of valence electrons in differently doped a-Si:H layers [1,2].

In a separate experiment, we study the chemical compositions of defective regions in thin film Si solar cells using energy-dispersive X-ray spectroscopy and EELS in the scanning TEM. We use nanometer-resolved chemical analysis to reveal the presence of ZnO in micrometer-long defective regions. We apply an unmixing algorithm to the EELS measurements to determine the chemical compositions of the defective regions objectively, without introducing artefacts from fitting procedures. The results obtained using this spectral decomposition procedure indicate that the defective regions in the Si layer are filled with ZnO, which diffuses along voids that propagate from the bottom of the absorber layer up to the top ZnO contact [3].

References
Electromigration-Assisted Interfacial Sliding at Hetero-interfaces

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In many modern engineering systems, such as miniaturized microelectronic chips and other micro- or nano-electro-mechanical devices, multiple materials are in intimate contact with each other while being subjected to extreme thermo-mechanical excursions and frequently, high current densities. This combination often results in unique scale sensitive near-interface phenomena, such as diffusively accommodated interfacial sliding, which may severely limit the life and performance of the system. Here, through some experimental work on model systems such as, thin metallic film lines on Si and Cu filled through Si-vias in microelectronic devices, we will show that the interfacial sliding at hetero-interfaces may occur under the combined actions of the interfacial shear stress (generated due to the mismatch between the coefficient thermal expansions of the adjoining components) and the electromigration. We find that the kinetics of sliding depends on the magnitude as well as the relative directions of the generated shear stress and the current density. We will discuss an analytical model of the phenomenon and the effect of substrate surface interlayers.
Thin Fe-Au bilayers (up to 20nm total thickness) were deposited by electron-beam deposition on sapphire substrates. The Au layer was single crystalline (with <111> normal to the substrate), while the Fe underlayer was polycrystalline and highly textured in-plane (with <110> normal to the substrate). Both atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) were employed to study the phase transformations after annealing in a temperature range of 600-900°C under a reducing atmosphere (Ar:H2 flow).

For very long annealing times (several days) solid-state dewetting leads to the formation of sub-micrometer sized particles. Under conditions for which two-phases (Au(Fe) and Fe(Au)) are in equilibrium, precipitation of Fe(Au) sub-particles occurs mostly on the facets of the Au(Fe) particle. These sub-particles exhibit a different equilibrium shape than of Au, resembling that of pure Fe, and grow with time until a bi-particle is obtained. Most importantly, during their growth the sub-particles are covered entirely by a thin Au layer, probably due to the reduction in surface energy.

A model was developed, demonstrating that the evolution of the bi-particle is governed by the minimization of total surface and interfacial energy. The model also takes into account the diffusion fluxes between the particle and the sub-particle. Implications for smaller particles and formation of a core-shell structure will be discussed.
Phase Distribution and Strain Analysis of LiFePO₄ / FePO₄ Interface by HAADF STEM Imaging

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Among a lot of cathodes of Lithium Ion Batteries (LIB), LiFePO₄ is one of the most promising materials with high theoretical electric capacity, high-temperature stability and good cyclic performance [1]. Previous studies showed that lithium insertion / extraction in LiFePO₄ is basically a two-phase process [2], that is, LiFePO₄/FePO₄ interfaces propagate through the bulk region with inserting/extracting lithium and electrons collectively. Obviously this two-phase mechanism should dominate entire battery properties, although detailed atomic structures of interfaces, and also related lithium & electrons collective diffusion, are still open questions. In this study, TEM & STEM observations were performed to characterize the two-phase interfaces, and we analyzed lattice strains and disordered interface structures at phase boundary in atomic scale.

Pristine LiFePO₄ powders were synthesized by solid state reaction. Powder XRD analysis showed there was only the LiFePO₄ single phase. Next, a chemical delithiation was performed (NOBF₄) in acetonitrile solvent. After this treatment, sharp FePO₄ XRD peaks were also appeared, which indicated both LiFePO₄ and FePO₄ phases were coexist. For TEM and STEM analysis, these particles were embedded in epoxy resin, thinned by mechanical polishing followed by Ar ion thinning under liquid nitrogen temperature.

TEM observations showed that the average particle size was of the order of µm, and most particles had core-shell structures (Fig. 1). Outer shells were highly distorted and cracked, while inner cores were almost free of defects. Diffraction patterns taken from each region strongly suggested that the outer shell was FePO₄, and the inner core was LiFePO₄. Considering the particle size and lattice constant mismatches, we concluded that cracks were introduced to accommodate lattice strains around the phase boundaries.

In STEM EELS line scan, the O-K edge pre-peak only appeared in outer shell (FePO₄), which originated from the differences in Fe-3d and O-2p mixing [3], and this pre-peak was disappeared near the end of the cracks. From this result, It was confirmed that phase boundaries were located very near at the end of the cracks, and the phase distributions were not affected by the specimen preparation procedure.

Atomic resolution HAADF imaging was also performed using C₅-corrected STEM, and we calculated strain fields by Geometrical Phase Analysis (GPA) method. Fig. 2 shows obtained εₓₓ and εᵧᵧ strain maps, in which we can find the clear phase interface with (100) and (4̅10) interface planes. Moreover, through line profiles of each strain maps, it was indicated that each strain map possessed different variation width, ~ 15 nm and > 60 nm in εₓₓ and εᵧᵧ, respectively. This result suggests that the LiFePO₄ / FePO₄ phase interface undergoes anisotropic lattice distortion, which should greatly affect lithium diffusion mechanisms in these regions.
Figure 1: The bright field TEM image for typical delithiated particle and (inset) corresponding diffraction pattern taken from whole particle.

Figure 2: (upper) The HAADF image and computed GPA strain maps (E_{xx}, E_{yy}, \omega_{xy}) represented in a dimensionless form. (lower) Line profiles of strain variations calculated from red rectangle regions.

References
A Model for Solid State Dewetting of a Fully-Faceted Thin Film

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Owing to their extremely high aspect ratios, most thin films are unstable and when they are heated, they will dewet or agglomerate to form islands. This process can occur in the solid state through capillary-driven surface self-diffusion. A key feature of the dewetting process is the retraction of the edges of the film, either natural edges, patterned edges, or edges where holes have formed. Models of edge retraction have been previously developed for isotropic materials and anisotropic materials with differentiable surfaces, but the effects of faceting in highly anisotropic materials have been largely unexplored.

We present a two-dimensional model of edge retraction for highly anisotropic, fully-faceted thin films. This model shows generally good agreement with experimental results for edge retraction of single-crystal Ni films on MgO. In both experiments and the model, rims form as the edges retract (Figure 1). The effects of adjusting various physical parameters on the edge retraction rate and the evolving rim geometry were explored using the model. The film thickness, surface self-diffusivity on the top facet of the rim, the equivalent contact angle of the film on the substrate (Figure 2), and the absolute value of the surface energies were found to be the factors that have the greatest influence on the edge retraction rate.

In isotropic models and some experimental systems, valleys form ahead of the retracting rims and deepen to contact the substrate and cause pinch-off. Our model suggests that this form of pinch-off will not occur when the rim is fully faceted and the top surface is an equilibrium facet. However, if a non-equilibrium top facet decomposes due to a faceting instability, valleys do form ahead of the rim and can lead to pinch-off (Figure 3). Otherwise, the only mechanism for pinch-off is uniform thinning of the film.

Figure 1: A retracting edge profile for a typical thin film with cubic symmetry is shown for various times after the annealing begins. The aspect ratio is 1:1, and the units of both the vertical and horizontal scale are micrometers.
Figure 2: The rate of edge retraction is affected by the equivalent film-substrate contact angle, \( \theta = \cos^{-1}\left[\left(\gamma_{SV} - \gamma_{SF}\right)/\gamma_{FV}\right] \), where \( \gamma_{SV} \) is the substrate-vapor interfacial energy, \( \gamma_{SF} \) is the substrate-film interfacial energy, and \( \gamma_{FV} \) is the film-vapor interfacial energy.

Figure 3: The retraction of a film with a sawtooth morphology on the top surface undergoes pinch-off by valley formation. This morphology typically occurs as a result of a non-equilibrium top facet undergoing a faceting instability. The scale bar at the bottom is in micrometers.
Deducing the Role of Functionalizing Macromolecules in the Nucleation of Colloidal Nanoparticles

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Macromolecules are commonly used during the synthesis of colloidal nanoparticles to prevent particle agglomeration. However, the details are not well understood for the formation of colloidal crystals in a solvent environment of high polymer concentration. Herein we present the results of experiments for elucidating this process.

Although polymers are widely employed to impart specific function to surfaces, techniques to characterize the adsorbed molecule are limited and usually indirect. We present two independent dynamic NMR studies to deduce the manner in which adsorbed poly-vinylpyrrolidone (PVP) attaches to the surface of ZnO colloidal nanoparticles and directs particle precipitation. In our colloidal system, the conformation of the polymer molecule on the particle surface—loosely described as trains, loops, or tails (see figure 1)—can be elucidated by probing the nuclear response of the solvent or the polymer to pulsed magnetic fields. The dynamic 1H-NMR signal of polymer-juxtaposed solvent molecules are monitored in our first approach, in which we monitor both spin-lattice (also known as $T_1$) and spin-spin (also known as $T_2$) relaxation behavior of the solvent, as the ease of solvent relaxation varies with proximity to the nanoparticle surface. In a second approach, the proton signal of the polymer is monitored over time. The rationale of this approach is that the signal of particle-bound polymer moieties will be lost faster than that of unbound polymer ones. Determining the signal of spin-echo and solid-echo processes enables calculation of polymer bound fraction.

The ZnO nanoparticle platforms are synthesized by the hydrolysis and condensation of zinc oxide precursors in PVP-containing solutions. Particle size distribution is determined by dynamic light scattering (DLS), as well as extrapolation from UV-visible absorption spectra. Three specific PVP concentrations are chosen in producing ZnO particles. Synthesis in solutions of high PVP concentration produces comparable results between the hydrodynamic radius and the extrapolated UV-visible radius, whereas at low polymeric concentrations, the difference between the two radii increases, suggesting a change in the conformation of adsorbed polymer on the nanoparticle surface under varying concentration. Dynamic NMR $T_1$ analysis reveals a loss of solvent mobility at higher polymer concentrations. These results imply that IPA becomes increasingly trapped in the polymer network and has more access to the particle surface at low polymer concentration. Although the particles differ in surface area, their bound fraction shows negligible variation. Additionally, $T_2$ analysis enabled calculations demonstrating that the bound fraction of polymer per nanoparticle unit surface area decreases with decreasing particle size. From these results, we conclude that at lower concentrations, PVP molecules appear to assume a tail conformation in which the head is strongly coordinated to the surface ions, while the rest of the molecule remains well-solvated.

In a separate experiment, we investigate the effect of the Zn precursor cations on the solvation of PVP, by using DLS to measure the hydrodynamic radius of entangled PVP in IPA, in the presence and absence of the zinc cation precursor. The results suggest that the zinc precursor ions pull the PVP chains closer, most likely due to the pyrrolidone rings on the polymers, and reduce the radius of gyration of polymer globules by 21% at high PVP concentrations. These results validate a model...
of highly dense polymer globules serving as reactors for ZnO nanoparticle precipitation, in which the high density of pyrrolidone rings in the globule hinders the diffusion of Zn\(^{2+}\) by electrostatic interaction. At high concentrations, large PVP globules appear to trap the reactant species and adsorb in a train conformation on the surface of precipitating ZnO nanoparticles. At low concentrations, the sizes of PVP globules are comparable to that of the evolving ZnO nanoparticles, and PVP adsorbs in looped and tail-only conformation. Due to the low entanglement of the polymer, the polymer globules are largely extended and interact with the ZnO surface significantly less.

![Figure 1: Possible polymer conformations onto the surface of particle](Image)

References

5. E. Alpaslan, H. Kurt, B. Yidiz, C.W. Ow-Yang, Dynamic NMR for probing the conformation of polymers functionalizing nanoparticles, under review
MACAN Young Scientist Abstracts

Poster Presentations
Studies of Compounds in the (ZnO)$_k$ In$_2$O$_3$ System for Thermoelectric Applications

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Thermoelectric materials gain considerable attention nowadays because of theirs ability to directly convert waste heat to electricity. They are described by a dimensionless figure of merit (ZT),

$$ZT = \frac{S^2 \sigma}{\kappa}$$

where $S$ is Seebeck coefficient, $\sigma$ electrical conductivity and $\kappa$ thermal conductivity. In order to achieve good values of ZT, high values of Seebeck and electrical conductivity are required together with maintaining low thermal conductivity. Conventional thermoelectrics are based on alloys of heavy elements, Bi, Te, Sb, Pb which have problems with stability in air in the temperature region above 300 °C. In contrast, thermoelectric oxide materials consisting of environmentally friendly and low cost constituents possess high stability in air at high temperatures. Among them, ZnO-based ceramics as an n-type material showed relatively good TE characteristics, especially when doped with In$_2$O$_3$ [1, 2].

The main goal of this research was to assess the influence of the amount of added In$_2$O$_3$ on the phase composition, microstructure and formation of structural defects in ceramics. We studied compositions in the homologous series (ZnO)$_k$In$_2$O$_3$ for $k = 5$, 11 and 18. According to TG/DSC and heating-stage microscope analyses, the reaction is occurring around 1150 °C and its further proceeding is strongly dependent on the initial composition. The samples were sintered in air in the temperature range from 900 °C to 1400 °C, from 2 hours up to several days. Thermally etched samples revealed planar defects and their control of grain growth direction with development of oblong shaped grains. All three compositions with different amount of dopant have similar microstructure. With HRTEM we observed modulated structure with a series of planar defects and a zig zag type defect in between (Figure 1), both formed by incorporation of In$^{3+}$ ion into ZnO parent structure. Planar defects are consisting of InO$_2$ octahedral layers acting as inversion boundaries. To obtain structure stability, there is another polarity inversion in between in In/Zn-O slab achieved with a zig zag defect type. Such structure has the influence on TE properties, as seen in Figure 2 with observed ZT values. The best results were obtained with composition for $k = 5$, with the highest amount of added dopant and consequently the largest amount of planar defects. The other two samples, with $k = 11$ and 18, have similar ZT values even with differences in the phase composition and structure.
Figure 1: Modulated structure in the (ZnO)$_m$In$_2$O$_3$ system with a series of InO$_2$ layers (inversion boundaries) with interim zig zag pattern in In/Zn-O slabs formed by incorporation of In$^{3+}$ into the ZnO parent structure.

Figure 2: Figure of merit ($ZT$) of the (ZnO)$_k$In$_2$O$_3$ system for compounds $k = 5, 11$ and $18$.

The microstructural and structural characteristics of the samples in the (ZnO)$_k$In$_2$O$_3$ system will be discussed with regard to the influence of the composition ($k$ value), microstructure, grain morphology, formation and ordering of the structural defects.

References
Tomography of a 3D Assembly of Silica-Based Nanotubes

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The functionalities of nanostructures depend strongly on their size and shape. Nanotubes are promising nanoobjects for diverse applications. In particular, the search for novel applications for one-dimensional silica nanotubes (NTs), e.g. in gas storage, drug/gene-delivery, sensing, catalysis or nanofluidic systems is a topic of great interest [1,2].

We found a synthesis route for a template- and solvent-free synthesis of silica-based NTs by solid-state chemistry [3]. Scanning Electron Microscopy (Fe-SEM, JEOL 6500-F) and Transmission Electron Microscopy (TEM, FEI Titan 80-300 kV S/TEM and 200kV FEI monochromated F20 UT Tecnai S/TEM) investigations evince two reaction products with different morphology, NTs and flakes (see figure 1). Both reaction products are amorphous in X-ray and electron diffraction. Energy dispersive X-ray and electron energy loss spectroscopy measurements showed that they differ in their chemical composition. The silica-based NTs consist mostly of silicon and oxygen whereas the flakes are dominated by phosphorus and nitrogen. The quantification of both products evinced that the atomic ratio Si : P was 4 : 1 for the NTs and 1 : 4 for the flakes indicating that the chemical composition influences the morphology. We are able to vary the average diameter and length of the nanotubes by changing the reaction conditions (e.g. temperature, Si amount). The silica-based NTs tend to form 3D networks. We are interested in the internal morphology of these networks as they may have the potential to act as molecular filters or nanofilters for separation or purification processes. Particularly, the porosity and connectivity of the silica nanotubes is significant for those applications. Therefore, the knowledge of their 3D structure is essential as a starting point to improve the material.

We recorded a tilt series on a nanotube fragment in STEM - High-Angle Annular Dark Field (STEM-HAADF) mode at 80 kV in a range of ±70° with steps of 10°. The reconstruction of the fragment was done by using the discrete tomography based on a masked simultaneous iterative reconstruction technique (SIRT) algorithm [4]. A calculated projection of the reconstructed NT fragment is shown in figure 2a. It indicates that the NTs are connected to each other. A cut through of the same 3D NT assembly prove that the NTs are hollow and that the junction points are open and connected, respectively (see figure 2b).

In conclusion, depending on the amount of silicon or phosphorus we can influence the morphology of the reaction products. Furthermore, we are able to control the diameter and length of the silica-based NTs. This is of high interest for further material development at nanoscale.
Figure 1: SEM image of the flakes and the silica-based nanotubes forming a 3D network.

Figure 2: (a) Calculated projection of the reconstructed nanotube 3D assembly and (b) a cut through of the same fragment.

References
5. Support by C. Minke (Department of Chemistry, LMU) for SEM analysis is kindly acknowledged.
Lithium, Niobium or Potassium-Doped TiO₂: Structural, Optical, Electrical and Electronic Changes

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TiO₂ is one of the most crucial components of Dye Sensitized Solar Cells (DSSCs) which functions as both charge separation and electron transfer layer (Figure 1). Therefore, manipulating the electronic, optical and structural properties of TiO₂ has attracted considerable attention. In order to have a better understanding on effect of doping on properties of TiO₂, undoped,Nb, K or Li doped TiO₂ nanopowders were synthesized using a bottom-up approach by sol-gel method. Structural changes in TiO₂ upon Nb, K or Li doping were followed with X-Ray Diffraction (XRD) and Raman Spectroscopy techniques. XRD results have shown that anatase to rutile phase transition is suppressed by Potassium (2 at%) and Niobium (6 at%) incorporation whereas it was facilitated by Lithium (2 at%). X-ray detectable binary phases were not observed in any of the cases. Additional Raman lines were observed at 362cm⁻¹, 323 cm⁻¹ and 242 cm⁻¹ for K or Nb doped anatase, which were missing in both Li-doped and undoped anatase TiO₂. This result indicates that symmetry of anatase is altered upon K or Nb doping whereas it is preserved by Li doping. Those additional lines might be attributed to brookite phase or the distortion of Ti-octahedra in anatase similar to Ti-octahedra of brookite. On the other hand, no substantial changes have been observed in the Raman Spectra of rutile. Nanopowders (K or Li-doped) were etched with hot sulphuric acid, in order clean the surfaces of the absorbed dopant ions. ICP-OES results of unetched and etched powders have shown that most of the K/Li could be on the surface of the particles and only 0.2% at K and 0.7% at Li has been incorporated into bulk anatase. In order to see the surface/bulk ion ratio, EDX measurements have been collected from different thicknesses of a wedge shaped specimen of Nb-doped powders (6 at%). No significant difference between the surface or bulk ion concentration has been found for the case of anatase.

Optical changes were followed with UV-Visible spectroscopy (Figure 2). K-doping and Li-doping have not resulted in a pronounced shift (389 and 388 nm, respectively) whereas Nb doping introduced a discernable redshift (412 nm) with respect to undoped anatase (387 nm). A similar trend has been observed for the case of rutile.EIS spectrum has revealed that Nb-doped rutile has a significant decrease both in the grain boundary and in bulk resistivities with respect to undoped TiO₂. In order to discern the differences introduced into the electronic structure of the host ceramic by Li, ELNES structures of pure lithium titanate phases of the Li₂O - TiO₂ equilibrium phase diagram (Li₄Ti₅O₁₂, Li₂TiO₃, Li₄TiO₄, Li₂Ti₃O₇) were investigated. Changes in the Ti-L₂,3, O-K, and Li-K signals (where available) were studied. It can be concluded that when considerable amount of dopants are present in the structure, bulk properties (structural, optical, electrical and electronic) show a significant change. However, with Li-doping, this has not been the case. These results indicate that the increase in efficiency of DSSC with Li doping is due to the surface effects, not due to the changes in the bulk properties.
Figure 1: Schematic representation of the processes taking place during DSSC operation.

Figure 2: UV-Visible spectra of undoped, Li,K or Nb-doped TiO₂. Purple and turquaz colored spectra reveal the changes due to Nb-doping.
Structure and Ionic Conductivity of Yttria-Stabilised Zirconia/Strontium Titanate Epitaxial Layers

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Nano-layered heteroepitaxial oxide systems have been shown to possess significantly enhanced ionic conductivities, which have been attributed to high interfacial mobility of the anions, as compared to those of the constituent materials in the bulk. A trilayer structure of 1 nm-thick epitaxial yttria-stabilised zirconia (YSZ) film sandwiched between strontium titanate (STO) layers [1] has garnered especially high interest with its reported 8 orders of magnitude enhancement in conductivity. This is a staggering improvement over the ionic conductivity of bulk YSZ; however, the nature of the conductivity observed in this system remains controversial to date.

Our work aims to provide the foundation for understanding the mechanism of ionic motion in such YSZ/STO heterostructures by first establishing the atomic structure at the interfaces. Based on indirect evidence from published high-resolution transmission electron microscopy [1], it has been assumed that the YSZ layer has an epitaxial fluorite structure. However, using energy dispersive X-ray (EDX) elemental mapping analysis of the cations in the system, we find presence of strontium and titanium elements within the YSZ layer (Figure 1). They appear to be located exactly in their respective perovskite lattice sites even in the YSZ layer, such that the cation perovskite lattice in the STO layer extends into the YSZ layer. In addition, zirconium shows a strong preference for the titanium equivalent lattice site within the YSZ 'perovskite' layer.

We compare this unexpected result with simulations of the interfacial structure of this system. We probe the energy landscape with a genetic algorithm in which the interatomic potentials are modelled with simple classical pair potentials [1], and explore possible low energy lattice structures of YSZ layers in perfectly coherent epitaxy with STO [3]. These configurations are identified and their energies evaluated with better accuracy based on density functional theory (DFT). We find that a fluorite structure of YSZ is mechanically unstable as an epitaxial layer between layers of STO. Instead, the genetic algorithm suggests a completely different phase, whose cation sublattice resembles that of a perovskite (Figure 2). This cation sublattice, at the same time, is identical to that of a fluorite. In this structure, we observe mixing between the STO and YSZ layers resulting in the presence of strontium and titanium within the YSZ layer, in agreement with the EDX results. Analysis of charge density of this new phase reveals that the charge compensating vacancies are not localised, but there are several small pockets of low charge density for each expected vacancy (Figure 2). Molecular dynamics (MD) simulations of this configuration reveal some relatively low barriers for anion diffusion; nevertheless, the activation energy for anion diffusion within the YSZ layer is predicted to be much higher than that of bulk YSZ. The results of this work therefore indicate that ionic conductivity of an ultra thin YSZ film in epitaxy with STO would be suppressed, in contradiction to some of the literature.
Figure 1: (a) High angular annular dark field (HAADF) image of a STO/YSZ/STO multilayer and the corresponding elemental maps of (b) Ti, (c) Sr, (d) Zr and (e) Y, showing the presence of Sr and Ti throughout the YSZ layer.

Figure 2: Simulated YSZ/STO layers showing the presence of strontium and titanium within the YSZ layer. The Zr$^{4+}$ ions are in light blue, Y$^{3+}$ royal blue, Sr$^{2+}$ green, Ti$^{4+}$ grey and O$^-$, red. Regions of low charge density are also indicated, shaded in dark purple.

References
Assembling “Smart” Ceramic Particles with Responsive Polymers to Build Complex Ceramic Structures

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This poster describes a novel bottom up approach to fabricate complex ceramic structures with controlled morphological features from macro to nano levels. The design of ‘smart’ inorganic particles by surface functionalization with responsive polymers allows us to reversibly trigger the self-assembly of ceramic emulsified suspensions to form cellular ceramics with complex structures and shapes.

Ceramic suspensions with solid contents ranging from 25-82wt% (up to 64vol%) were emulsified and their rheological behaviour was evaluated as a function of their composition. This work will describe the processing of ceramics using functionalized ceramics and its relationship to the morphology and microstructure of the sintered materials with particular emphasis in density, pore size, pore shape and strut thickness. The mechanical properties (flexural and compressive strengths) were also evaluated. Alumina foams with closed porosities ~60 vol% can exhibit compressive strengths of ~250 MPa in the upper range for this type of materials. Our preliminary results show that this procedure is a promising path to fabricate strong, porous ceramics with complex shapes.
The Influence of Carbon Nanostructures on the Sintering of ZrO₂

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In the present work, we study the influence of graphene oxide (GO) in the sintering and grain growth of partially stabilised zirconia (ZrO₂). Graphene oxide was prepared through the exfoliation of graphite following a modified Hummers method. In order to obtaining a homogeneous GO dispersion in the ceramic matrix, we used a wet processing route to prepare GO/ceramic composites with different graphene oxide contents below and above the percolation threshold. Sintering of the composites was carried out by Spark Plasma Sintering (SPS), that allows rapid high temperature processing without degrading the carbon phase and minimizing the grain grow. The composites were sintered using a 200 °C/min heating rate and maximum temperatures between 1200 and 1350 °C applying low pressure. The composites exhibit a uniform structure and the reduction of GO to graphene after sintering has been evaluated and confirmed by Raman spectroscopy. The SPS apparatus allowed us to record the sintering kinetics under isothermal conditions. The data has been used to identify the dominant sintering mechanisms and calculate the corresponding activation energies. The experiments suggest that GO inhibits grain growth and adds a new sintering stage at low densities akin to flow-controlled densification. The results have been compared with the effect of other carbon structures: carbon nanotubes (CNT). The comparison is used to identify common phenomena and outline key differences in the sintering mechanisms and the microstructure of the final materials.

Figure 1. Fracture microstructure of GO-ZrO₂ composite.
In-situ Au Deposition and Formation of Droplets on (100) III-V Substrates by Molecular Beam Epitaxy

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As a preface for nanowire growth, catalyst particles of desired size, density, and composition need to be prepared on the growth substrate. We have investigated an in-situ Au particle deposition method which insures that no impurities are present in the catalyst. The Au particles are prepared by first degassing the substrate to remove oxide and other contaminants, then a buffer layer is grown to obtain an uniform and reproducible (100) surface, and finally a thin layer of Au is evaporated onto the substrate from a Knudsen cell placed in the MBE growth chamber. The evaporated Au layer merge, what appears to be immediately, into nm sized particles.

Prior to Au evaporation the substrate is a perfect (100) surface. However, the Au alloys with the substrate and forms an Au/group-III particle (almost no group-V atoms are present in the particle). The alloying also creates new surface facets as the catalyst/substrate system seeks to minimize the energy.

In a SEM with in-situ Gallium ion-miller, we have cut through multiple alloy particles along the [110] and [1-10] substrate directions. The cuts have allowed us to investigate what interface surfaces have formed between the particles and the substrate. The found interfaces, the relation between their lengths in the 2D cuts, and the particle volume have been used as constraints in Wullfmaeker’s\textsuperscript{1} double-Winterbottom construction to extract the relationship between the interface energies.

It is important to note that the particles have been investigated after extraction from the growth system. Both during evaporation and under subsequent nanowire growth the catalyst particle will be liquid, and the values found here are for solid particles at a different temperature and pressure.
Figure 1: Effect of substrate temperature on Au deposition on GaAs(100). By raising the temperature of the substrate during Au evaporation the density of the catalyst particles is decreased and the size of the individual particle is increased.

Figure 2: Above: Side view of Au/Ga particles on GaAs(100) surfaces. Below: The equivalent side views calculated using Wulffmaker with a AuGa solid particle on GaAs.

References
Solid-State Dewetting and Pt-SrTiO$_3$ Interfaces

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Solid-state dewetting has become a common method for “bottom-up” processing, such as for producing catalyst particles and nanocrystals (NCs) for memory devices [1-4]. As such it is very important to understand the kinetics and mechanisms of solid-state dewetting, and to correlate these parameters with the structure, chemistry and energy of the interfaces in these systems.

Most studies on nonvolatile memories (NVM) based on metal NCs have focused on finding the best dewetting parameters defined by measured electrical properties. However, understanding the kinetically dependent physical mechanism by which dewetting occurs, and how it depends on the interface structure and chemistry which define the thermodynamic driving force for dewetting (interface energy and equilibrium crystal shape), were not studied in detail.

The main goal of this research is to experimentally determine the kinetics and mechanisms of solid-state Pt dewetting as a function of surface perturbations, reconstruction, and surface/interface chemistry.

In this study, surface reconstruction of (001) SrTiO$_3$ was characterized using aberration corrected high resolution transmission electron microscopy (HRTEM) and exit wave reconstruction. Annealing (dewetting) was conducted at 1150°C under a low partial pressure of oxygen (P(O$_2$)=10$^{-25}$) on two samples, a (001) STO substrate with a TiO$_2$ termination (figure 1a) and a (001) STO substrate with a TiO$_2$ termination coated with a Pt thin film to form nanometer length-scale particles (figure 1b). In addition to the equilibrated Pt particles, anisotropic lateral features were visible on the surface of the substrate and at the interface while on the bare STO sample TiO$_2$ termination is clearly seen as anisotropic terraces. These results imply that the Pt serves as a catalyst which reduces the STO substrate to a reduced form of strontium oxide due to the low partial pressure of oxygen.

Furthermore, annealing of STO coated with a Pt thin film was conducted at 1150°C using different P(O$_2$). At low partial pressures equilibrated Pt particles were located on the reduced substrate, while under a high partial pressure of oxygen no reduction was observed. However, terraces are seen in between the equilibrated Pt particles (figure 2).
Figure 1: (a) HRSEM micrograph of an (001) SrTiO₃ sample with TiO₃ termination annealed at 1150°C for 2hr in Ar+H₂. (b) HRSEM micrograph of the dewetted particles and the reduced substrate annealed at 1150°C for 10hr in Ar+H₂.

Figure 2: SEM micrograph of the Pt particles dewetted at a high partial pressure of oxygen.

References
Ni-YSZ(111) Solid-Solid Interfacial Energy

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The stability of metal films on oxide surfaces is important for the performance of devices such as solid oxide fuel cells (SOFCs) and thermal barrier coatings (TBCs) [1-3]. Ni-YSZ serves as an anode material in SOFCs. During SOFC operation, the metal-ceramic interface is subjected to high temperatures and a reducing atmosphere, which can lead to coarsening of the Ni nanoparticles, which decreases the number of three-phase boundaries. The three-phase boundaries (Ni/YSZ/fuel-gas) are essential for catalytic activity which controls the electrical properties. A better understanding of the equilibrated Ni-YSZ interfacial structure and energy can lead to improved adhesion and long-term stability of SOFCs [4,5].

In this work, agglomeration ("dewetting") of thin Ni films on YSZ substrates was studied. The orientation distribution of the Ni particles on the substrate was examined using X-ray diffraction (XRD). The equilibrium crystal shape (ECS) of the Ni crystals was determined and the interfacial structure was investigated using high resolution scanning and transmission electron microscopy (HRSEM, HRTEM). The solid-solid interfacial energy was measured using Winterbottom analysis, and was determined to be 1.9±0.2 J/m² at T=1350°C (0.93 Tm, Ni), P₀₂=10⁻²⁰ atm. The OR found was Ni[T10](111) // YSZ[T10] (111).

Figure 1: High angle annular dark field STEM micrograph of a Ni particle equilibrated on a (111) YSZ substrate. Inset is the interface viewed by phase contrast TEM.

References
Anisotropic Grain Boundary Mobility in Undoped and Ca Doped α-Alumina

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The equilibrium phase of alumina (α-Al₂O₃) has a variety of applications, such as in bio-medical implants, diffusion barriers for high temperature applications, and applications requiring good wear resistance. The mechanical and functional properties of polycrystalline alumina strongly depend on the microstructure, which in part depends on grain growth during sintering.

At this point it is accepted that dopant segregation to grain boundaries results in a solute drag effect, reducing the mobility and the rate of grain growth. However, recent studies [1,2] of various systems have shown that dopants segregating to grain boundaries actually increase the grain boundary mobility, although it is not clear if the samples were doped below the solubility limit.

In order to achieve a better understanding of the microstructural evolution during sintering, the influence of Ca on grain growth below the solubility limit was studied. Pure and 15 ppm Ca-doped polycrystalline alumina samples were prepared from highly pure powders (99.99%). The polycrystalline alumina samples were then diffusion bonded to (0001) single crystals at various annealing temperatures and times.

For the undoped samples the grain size was measured after annealing at 1600°C, 1650°C and 1700°C for times of 36, 48 and 60 hr. The grain size of the Ca-doped samples was measured at 1600°C for various annealing times of 5, 10, 25, 30, 40, 50 and 60 hr. (see figure 1).

The results show a clear trend of enhanced grain growth for the polycrystalline samples compared to the C-plane oriented single crystal due to the low grain boundary energy defined by the basal plane. The effective mobility was measured for all samples (see figure 2).

Moreover, it is shown that adding Ca below the solubility limit (which is 51 ppm at 1600°C) results in enhanced grain growth compared to the undoped samples at earlier stages, and therefore a higher mobility. After extended annealing times the grain growth rate decreased.
Figure 1: Grain size versus time for (a) polycrystalline undoped and Ca-doped alumina, and (b) C-plane undoped and Ca-doped diffusion bonded samples.

Figure 2: Effective grain boundary mobility versus inverse temperature for undoped, Ca doped polycrystalline alumina, C-plane sapphire bonded to undoped alumina, and C-plane sapphire bonded to Ca-doped alumina.

References
The Mechanisms of Grain Boundary Motion

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The kinetics of grain boundary (GB) motion can be experimentally determined, and thus the mobility of GBs can be extracted. However, the mechanism by which a GB migrates has not yet been determined. Some models were proposed to account for experimental observations, however none of the models were confirmed by experimental atomistic studies of the boundaries in question.

One of the models for the GB motion is the terrace ledge kink (TLK) model originally developed to describe crystal growth at solid-liquid or solid-vapor interfaces [1]. It was suggested by Gleiter [2,3] that a grain is terminated by steps which are the source of GB motion. In his model Gleiter suggested that the process of GB migration in the absence of segregation is via diffusion of atoms to the grain surface, then atoms diffuse along the surface, attach to step sites, and finally diffuse along the step into a kink site.

Thus, the mechanism of GB migration is being studied where steps, which following the TLK model, are hypothesized to be the active mechanism for GB motion. SrTiO3 was selected as a model system due to its semi cubic structure (pervoskite), enabling easier interpretation of the mechanism by electron microscopy.

In order to fully understand the mechanism, the kinetics of the GB involved should be well known. Therefore the kinetics of the GB motion in SrTiO3 is taken from the work done by Baurer et al. who showed that the "effective mobility" $2\gamma/\mu$ is reduced at two distinct temperatures by orders of magnitude with increasing temperature [4]. This behavior deviates from the expected Arrhenius type behavior, and is independent of the Sr/Ti ratio of the ceramic.

Nanometric steps were detected at GBs in polycrystalline SrTiO3 (Fig. 1) using high resolution transmission microscope (HRTEM), where the GB is identified according to changes in the lattice image acquired while the GB is parallel to the incident electron beam (edge on). The TEM samples were made from a polycrystalline SrTiO3, sintered at different temperatures by Baurer et al. from a mixture of SrCO3 and TiO2 powders.
Figure 1: HRTEM micrograph of an edge-on GB under negative Cs conditions. The upper grain is in a [001] zone-axis. Nanometric steps are visible along the boundary.

Since a TEM micrograph is the result of convolution of the exit wave function (of the electron beam immediately after passing through the sample) and the contrast transfer function (CTF) of the microscope, it is impossible to extract the atomistic structure from a single image without additional information. Thus, simulations of TEM images from GBs were made using a software package [5] on GBs that were constructed using Crystal Maker [6]. For each GB the simulated specimen was cut (in the direction of the electron beam) to assure that the weak phase approximation applies, and the dynamically scattered electron wave was convoluted with the CTF of the Technion Titan. Negative Cs conditions [7] were chosen (Fig. 1) since under these conditions white contrast in the micrograph coincide with the position of atomic columns and minimum delocalization is achieved [8]. By using this kind of simulation it is possible to solve the atomistic structure from a micrograph by comparing simulated images with the experimentally acquired micrograph.

References
Structural and Thermodynamic Characterization of Pt-SrTiO₃ Interfaces

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Metal and metal oxide nanoparticles have recently gained importance in many modern applications such as catalysts, sensors, microelectronics, anti-corrosive or water repellent coatings, antibacterial agents and many more. Nanoparticles owe their special properties to the fact that a relatively large portion of the atoms are at or near the surface. Many of the properties of nano-crystals are dictated by their thermodynamic state, including their equilibrium crystal shape, interface energy, etc.

A better insight into nano-particles can be achieved by experimentally determining their equilibrium crystal shapes, measuring the interface energy between the particles and single crystal substrates [1], and by determining the atomistic structure at the interface (and surfaces).

Pt on (001) single crystal SrTiO₃ substrates was selected as a model system for this study, due to the fact that there is a very small lattice mismatch (~0.4%) between these two crystals and a cube on cube orientation was expected.

Equilibrated Pt particles on the substrate were achieved by evaporating Pt thin films on the chemically-treated substrate and dewetting in the solid-state. The results show that the annealing atmosphere plays an important role on the particle-substrate interface. In addition, it appears that the Pt-SrTiO₃ orientation is more complicated than expected.

Figure 1: Micrograph (a) shows Pt nanoparticles dewetted on a SrTiO₃ substrate in an Ar+O₂ atmosphere at 1150°C for 10 hours. (b) shows a pole figure of {111} planes of Pt. Both figures shows lack of in-plane preferred orientation.

XRD and EBSD analysis shows that most of the Pt particles have (111) planes parallel to the substrate surface, however, there is no definite preferred in-plane orientation relationship, which suggest that the Pt-SrTiO₃ interfacial energy is isotropic about the (111) preferred orientation.
Figure 2: TEM bright field micrograph of an equilibrated Pt nanoparticle on SrTiO₃.

One of the possible explanations to the lack of a defined low-index orientation relationship is the morphology of the substrate. SrTiO₃(100) has a cubic perovskite structure and it has two possible terminations with surface compositions of SrO or TiO₂. DFT calculations showed that the Pt interface with the TiO₂-terminated surface is more stable than with the SrO-terminated surface [2-3]. For this reason, SrTiO₃(100) substrates were chemically treated [4] prior to Pt film deposition, in order to form a uniform TiO₂ termination. After thermal equilibration this chemical treatment of the substrate creates multi-layered terraces on the surface. It may be that the presence of these terraces cancels the expected cube-on-cube orientation relationship, especially when particles are located on more than one terrace.

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The Role of Grain Boundary Diffusion in Solid State Dewetting of Thin Iron Films on Sapphire

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Solid state dewetting of the thin metal films on the ceramic substrates is a transformation of thin continuous film into array of isolated particles controlled by diffusion processes in or on the solid metal. This process can serve as a tool for producing of ordered nanoparticle arrays for optical/magnetic applications and for catalytic growth of nanowires and nanotubes. This increasing technological importance of thin film dewetting drives the need for fundamental studies of the underlying physical mechanisms and kinetics responsible for it.

We studied the initial stages of solid-state dewetting of 25 nm-thick Fe films on basal plane-oriented sapphire substrates. The dewetting process occurred via nucleation and growth of through-thickness craters within the film. The rims along these voids were not elevated, in contrast to commonly observed void growth mechanisms. Instead, the material that was consumed during the crater expansion was absorbed by several isolated grains in its vicinity but not adjacent to it. These grains transformed into faceted hillocks that protruded above the original film surface at later stages. A thin film dewetting model is proposed, in which the self-diffusion of Fe atoms along the grain boundaries transports the mass from the expanding cavities to the hillocks and determines the kinetics of this dilation. The grain boundary self-diffusion coefficients of Fe that were estimated based on the experimentally determined crater expansion rates and the proposed model agreed well with the values in literature.
STEM Observation of Dopant Distributions along the $\{11\overline{2}0\}/<1\overline{1}00>2^\circ$ Low-angle Tilt Grain Boundary of Alumina

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Dopant atoms in a crystal are known to segregate to dislocations and form so-called Cottrell atmospheres to accommodate strain fields around dislocations. In addition, dislocations act as rapid diffusion paths of dopant atoms, which is known as pipe-diffusion phenomenon. It has been shown that these characteristic properties of dislocations can be used to form novel nano-scale structures inside oxide materials. For instance, conductive Ti-rich nanowires in insulating sapphire single crystals have been fabricated by dislocations [1]. However, fundamental mechanisms of dopant segregation at dislocations are not well understood yet, especially in oxide materials, mainly because the difficulty in controlling dislocation structures. Here, one successful method for introducing dislocations into crystals is the fabrication of low-angle tilt grain boundaries by bicrystal method. With this method, several dislocation structures can be introduced in nanometer order by controlling crystallographic orientations of two crystals; therefore, these model dislocation structures are convenient for studying the interaction between dislocations and dopant atoms systematically. In a $\{11\overline{2}0\}/<1\overline{1}00>2^\circ$ low-angle tilt grain boundary of alumina, a periodic array of climb-dissociated basal edge dislocations with stacking faults (SF) in between is introduced according to following equation [2].

$$1/3<11\overline{2}0> \rightarrow 1/3<10\overline{1}0> + SF + 1/3<01\overline{1}0>$$

The core structures of those dissociated partial dislocations have been observed by scanning transmission electron microscopy (STEM). It was found that the upper partial dislocations and the lower partial dislocations were terminated by -Al-Al columns and -Al-O columns respectively, and being locally nonstoichiometric [3].

In this study, five kinds of metal ions (Ni$^{2+}$, Sr$^{2+}$, Er$^{3+}$, Zr$^{4+}$ and Ti$^{4+}$) are doped into the low-angle tilt grain boundaries of alumina to understand the dopant segregation behaviors around partial dislocation cores. Figure 1 shows a bright field TEM image of the Er-doped grain boundary. All the metal doped grain boundaries consisted of periodical arrays of $b=1/3<10\overline{1}0>$ and $b=1/3<01\overline{1}0>$ partial dislocation pairs with SF in between. These dislocation structures were consisted with that of the undoped ones. Figure 2 shows a low-magnified HAADF-STEM image of the Er-doped grain boundary. Periodic brighter contrast due to the presence of Er atoms can be confirmed along the grain boundary. Atom-resolved Z-contrast STEM images revealed that all of the five kinds of dopant atoms segregated in the vicinity of the dislocation cores but not to the SF regions. The segregation amount ratio to the upper/lower partials is likely to depend on valence states of dopant atoms, but not on the ionic radii. Namely, we found that the upper partials tend to attract divalent cations, while the lower partials tend to attract tetravalent cations. These results suggest that the partial dislocation cores may be locally electrically charged; and thus, electrical interactions
between dislocation cores and dopant atoms must be the key to understanding the dislocation segregation mechanisms in alumina.

Figure 1: A Bright-field TEM image of the Er-doped grain boundary. An array of partial dislocation doublets can be seen.

Figure 2: Low-magnification HAADF-STEM image of the Er-doped grain boundary. Periodic brighter contrast due to the existence of Er atoms can be seen.

References
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