DS 21: Thin Film Characterisation: Structure Analysis and Composition II

Time: Tuesday 9:30–13:00 Location: CHE 91

DS 21.1 Tue 9:30 CHE 91

Analysis of domain formation of epitaxial chalcogenide thin films — •Marc Pohlmann[1], Marvin Kaminski[1], Matti Wirtssohn[1], Abderaffi Moktad[1], Oana Cojocaru-Mirédin[1], Peter Jost[1], and Matthias Wuttig[1,2] — [1]I. Institute of Physics, Physics of New Materials, RWTH Aachen University, 52056 Aachen, Germany — [2]Sommerfeldstr. 14

Many chalcogenide alloys can be employed in phase-change memories because their optical and electrical properties differ strongly between their crystalline and amorphous phases. Interest in highly-textured or even epitaxially-grown chalcogenide thin films is fueled by the recent discovery of the advantageous memory-switching properties of chalcogenide superlattices, so-called interfacial phase-change memories (IPCMs), as well as by the topological properties of such films. High quality thin films can be produced by molecular beam epitaxy. However, in many material systems different rotational domains lead to the formation of grain boundaries or twin defects. To reduce these defects, it is essential to understand why and how the different domains are formed.

Therefore, in this work we combined electron backscattering diffraction (EBSD) with XRD to attain a sound understanding of the local domain structure and the mechanisms of domain formation in MBE-grown chalcogenide thin films.

DS 21.2 Tue 9:45 CHE 91

Growth and characterization of VO$_2$ thin films deposited on various perovskite and complex oxides single crystal substrates — •Adrian Petraru[1], Gabriel Bello Waldschütz[1], Ravi Droopad[2], and Hermann Kohlstedt[1] — [1]Nanoelektronik, Technische Fakultät, Christian-Albrechts-Universität zu Kiel, Kiel, Germany — [2]Texas State University, Ingram School of Engineering, San Marcos, TX 78666 USA

Correlated electron materials exhibiting first-order metal-insulator phase transitions (MIT) accompanied by an abrupt change in the resistivity over several orders of magnitude have recently attracted considerable attention for applications in the field of non-volatile memories due to their sub-nanosecond transition timescale and electrical read-out scheme. Oxide multilayer heteroepitaxy combining VO$_2$ films and conducting/ferroelectric/dielectric films open new opportunities in creating functional devices. VO$_2$ thin films were deposited on various single crystal complex oxide substrates compatible with ferroelectric PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) and BaTiO$_3$ thin films using pulsed laser deposition method. Thus, SrTiO$_3$(100), PZT/SrRuO$_3$ buffered SrTiO$_3$(100), SrTiO$_3$S buffered Si(100) substrates, NdGaO3(110), MgO(100), PZT/SrRuO$_3$ buffered GdScO$_3$(110), and PMN-PT(001) substrates were used in combination with VO$_2$ films. The deposited VO$_2$ films were structurally charaterized by X-ray diffraction and Raman scattering spectroscopy. Electrical measurements show a change in resistance of the VO$_2$ across MIT ranging from 10^2 to 10^4 times.

DS 21.3 Tue 10:00 CHE 91

Microstructural properties of Ti2AlN MAX-Phase thin films, synthesized by multilayer PVD techniques — •Lukas Gröner, Eduart Reisacher, Eberhard Nold, Alexander Fromm, Frank Meyer, Chris Eberl, and Frank Burmeister — Fraunhofer IWM, Freiburg, Deutschland

Mn+1AXn phases belong to a group of ternary nitrides or carbides, where M denotes an early transition metal, A denotes mostly a group III or IVA element and X is either nitrogen or carbon. In recent years, an increasing number of investigations on the synthesis and characterization on crystalline Mn+1AXn phases have been published which focus on their suitability for industrial applications, e.g. as protective coatings. Due to the mixture of strong covalent MX bonds and weak ionic MA bonds, these materials often exhibit a high corrosion resistance as well as good electrical conductivity and thermal stability. However, these properties strongly depend on the material*s crystallinity. Ti2AlN MAX-phase thin films were synthetized on various substrates in a reactive sputter mode by a multilayer-deposition of AlN and Ti single layers under variation of the double layer thickness, followed by a subsequent annealing step. The synthesis results were investigated by elemental analysis and electron microscopy. The evolving microstructure with a preferential orientation in the texture was analyzed by polarized Raman spectroscopy and XRD. Besides temperature and annealing time, the double layer thickness turned out to be a key parameter to adjust the orientation and grain size.

DS 21.4 Tue 10:15 CHE 91

Characteristic Diffuse Scattering from Rough Lamellar Gratings — •Analia Fernandez Herrero[1], Victor Soltwisch[1], Mika Pflüger[1], Jürgen Probst[2], and Frank Scholze[1] — [1]Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin, Germany — [2]Helmholtz-Zentrum-Berlin (HZB), Albert-Einstein Str. 15, 12489 Berlin, Germany

Lamellar-gratings are commonly-used diffractive optical elements or structural elements in state-of-the-art integrated electronic circuits. For the control of the lithographic manufacturing process a rapid inline characterization of such structures is indespensible. There are numerous reports on the determination of the geometry parameters of such gratings from optical and EUV light scattering. With shrinking structure sizes, roughness gains influence on the structure performance. Its characterization by scatterometry requires to identify the roughness contributions. For lamellar gratings, roughness is clasified as line width roughness (LWR) or line edge roughness (LER). We prepared a set of eight Si-lamellar gratings with well defined LER or LWR and a prototype grating by e-beam lithography at HZB. The samples were investigated at PTB using EUV-scatterometry, which is very sensitive to the imperfections on the structures and therefore provides a high sensitivity for roughness. We observed that each type of line roughness leads to a characteristic diffuse scattering pattern, with strong correlation between the type of roughness and the diffuse scatter angular distribution. The analysis of these diffuse scatter contributions opens a new path for the roughness characterization of line structures.

DS 21.5 Tue 10:30 CHE 91

Structure-property relationships in catalysts identified by combining data science and high-throughput experimentation — •Helge S. Stein[1], Jinjang Li[2,3], Ramona Gutkowski[4], Christina Eberling[1], Sally Jiao[5], Kirill Sliozberg[4], Christoph Schwanke[6], Karin M. Aziz-Lange[6], Lifei Xi[6], Andre D. Taylor[2,3], Wolfgang Schuhmann[4,7], and Alfred Ludwig[1,7] — [1]Institute for Materials, Ruhr-Universität Bochum — [2]Department of Chemical and Environmental Engineering, Yale University — [3]Center for Research on Interface Structures and Phenomena, Yale University — [4]Analytical Chemistry-Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum — [5]Department of Chemical and Biological Engineering, Princeton University — [6]Operando Characterization of Solar Fuel Materials, Helmholtz-Zentrum Berlin für Materialien und Energie — [7]ZGH & MRD, Ruhr-Universität Bochum

The transition towards a zero-CO2-emission economy requires clean and renewably produced fuels such as hydrogen. In this contribution, catalysts for the efficient production of hydrogen through water reduction (HER) and oxidation (OER), as well as catalysts for the reverse reaction, namely oxygen reduction (ORR), will be shown. Through the implementation of versatile machine learning and statistical methods, novel structure-property correlations were discovered from a total of over 1500 synthesized compositions. These findings offer possible search strategies for the discovery of new and improved catalysts. As an outlook, high-throughput XPS analysis on Co-Fe-Mn-O will be demonstrated.

DS 21.6 Tue 10:45 CHE 91

Combining human and algorithmic analysis for the rapid identification of phase regions and crystal structures — •Helge S. Stein[1], Sally Jiao[2,1], and ALFRED Ludwig[1,3] — [1]Institute for Materials, Ruhr-Universität Bochum, — [2]Department of Chemical and Biological Engineering, Princeton University, — [3]ZGH & MRD, Ruhr-Universität Bochum

A major challenge in combinatorial materials science remains the efficient analysis of X-ray diffraction (XRD) data and its correlation to functional properties. A rapid identification of phase regions and proper assignment of corresponding crystal structures is necessary to keep pace with the improved methods for synthesizing and characterizing materials libraries. Therefore, a new modular software called htAx (high-throughput analysis of X-ray and functional properties data) is presented that couples human intelligence tasks, used for "ground-truth" phase-region identification, with subsequent unbiased verification by a peak-matching algorithm in order to efficiently analyze which phases are present in a materials library. Identified phases and phase regions may then be correlated to functional properties in an expedited manner. To demonstrate the functionality of htAx, two previously published XRD datasets of the materials systems Al-Cr-Fe-O and Ni-Ti-Cu are analyzed by htAx. The analysis of about one-thousand XRD patterns takes less than one day with htAx. The proposed method reliably identifies phase-region boundaries and robustly identifies multiple phases.

DS 21.7 Tue 11:00 CHE 91

Analysis of surface oxidation of TiON ALD films — Justyna Łobaza, •Małgorzata Kot, and Dieter Schmeisser — BTU Cottbus-Senftenberg, Konrad-Wachsmann-Allee 17, 03046 Cottbus

Titanium oxynitride (TiON) films are interesting due to their remarkable optical and electronic properties which strongly depend on the O/N ratio. However, it is known that films containing Ti are prone to oxidation in contact with the air [1]. In this work, we study the thickness of a surface oxidation layer which is inherently formed on the atomic layer deposition (ALD) grown TiON/TiN films on Si substrate. We use an Ar^+ ion bombardment source and X-ray photoelectron spectroscopy (XPS) for this analysis. We calibrate the sputter rate by using substrate signal intensity decay (here Si 2p) in the XPS spectra of the 5 nm thick TiON sample accordingly. This rate is assumed to be constant when films with a larger thickness are analyzed. We find that the surface oxidation layer is about 1 nm thick, independent on the detailed ALD parameters of the films. The TiN films found underneath are close to the stoichiometric values and have a residual O content below 5%. Finally, we compare these data to our previous results collected with synchrotron-based radiation source [2,3].

References: [1] Sowinska et al., Applied Physics Letters 100, 233509 (2012). [2] M. Sowinska et al., Applied Surface Science 381, 42-47 (2016). [3] M. Sowińska et al., Journal of Vacuum Science and Technology A, 01A12734 (2016).

15 min. break.

DS 21.8 Tue 11:30 CHE 91

Interfacial oxide formation during ALD oxide growth on reactive metals for resistive switching devices — •Stephan Aussen, Alexander Hardtdegen, Katharina Skaja, Regina Dittmann, and Susanne Hoffmann-Eifert — Peter Grünberg Institut (PGI-7) and JARA-FIT, Forschungszentrum Jülich, 52425 Jülich, Germany

In this study we investigate the oxidation behavior of different metals (M) including Hf, Ta and Pt during atomic layer deposition (ALD) of stoichiometric oxide films (M′O) including Al_2O_3, TiO_2 and HfO_2 and the switching behavior of the resulting stacks. The 25 nm thick dense metal films with low surface roughness < 0.3 nm were grown on thermal oxidized Si wafers in an off-axis sputter tool with a base pressure $< 10^{-10}$ mbar. The hexagonal Hf films and the cubic Pt films show (002) and (111) textures, respectively. In contrast, the Ta films consist of a mixture of the α- and β-tantalum phase. All metal films were transferred under ultra-high vacuum into an ALD plasma system. 3 nm thick oxide layers were deposited at 300 °C using O_2-plasma as the oxygen source. The resulting stacks were investigated by x-ray photoelectron spectroscopy to study the oxidation of the metal surface due to the oxide deposition. In addition, complementary resistive switching experiments were performed on equivalent stacks, i.e. $Pt/M'O/MO_x/M$. The influence of the in-situ formed metal oxide interface (MO_x) on the switching behavior of the stacks is discussed.

DS 21.9 Tue 11:45 CHE 91

Analytical Electron Microscopy Study to Resolve the Phase Morphology of Organic Solar Cell Blends — •Mona Sedighi[1,2], Markus Löffler[1], Petr Formanek[2], and Ehrenfried Zschech[3] — [1]Dresden Center for Nanoanalysis, Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden — [2]Leibniz-Institut für Polymerforschung Dresden e.V., Dresden — [3]Fraunhofer-Institut für Keramische Technologien und Systeme (IKTS), Dresden

To increase the efficiency of bulk heterojunctions for organic photovoltaic devices (OPV), the complicated photon-to-electron conversion process has to be understood in detail. Most OPV consist of a single bulk-heterojunction active layer; the blend of electron donor (conjugated polymer) and electron acceptor (fullerene) which makes an interpenetrating network of domains, ideally on the length scale of the exciton diffusion length. Therefore, morphology of the active layer significantly contributes to the overall performance of OPV.

Obtaining insights into the morphology of the active layer requires the spatial resolution and a contrast mechanism to discriminate two phases with similar average atomic number. To tackle this challenge, we combine electron microscopy imaging with different analytical techniques; energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) in TEM. We imaged different phases of the donor and acceptor, forming ordered and non-ordered regions, depending on the way the heterojunction is fabricated.

DS 21.10 Tue 12:00 CHE 91

Quantitative Raman spectroscopy of doped and undoped multiphase TiO_2 thin films on complex substrates — •Sebastian Schipporeit[1,2,3], Dieter Mergel[1], and Volker Buck[1,2] — [1]Thin Film Technology Group, Faculty of Physics, University Duisburg-Essen — [2]CENIDE, Duisburg — [3]University of Wuppertal, School of Mechanical Engineering and Safety Engineering, Material Technology, Wuppertal

We have developed a method that allows a quantification of crystal structures in thin films on complicated substrates with Raman spectroscopy. This method was applied to pure and Nb-doped TiO_2 thin films, deposited by various coating techniques onto B270 glass. The films were deposited or post-heated between 60 °C and 650 °C Raman maps were created within areas of 30 x 30 μm in 250 nm steps. This gives the possibility to determine the spatial distribution of crystal phases within the films and to enhance the signal to noise ratio. We decompose the spectra into the two main components substrate and film, and furthermore the spectrum of the film into an amorphous content, crystalline backgrounds and, finally, the Raman peaks of the various crystal phases. Modelling the whole spectrum eliminates any arbitrary background allowing even small traces of crystalline phases to be detected. The films contain amorphous, anatase, rutile and brookite structures.

DS 21.11 Tue 12:15 CHE 91

Improved XPS Background Fitting with a Modified Tougaard Universal Cross Section Using the Example of Aluminium — •Manuel Monecke, Georgeta Salvan, and Dietrich R.T. Zahn — Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

X-ray photoelectron spectroscopy (XPS) spectra are commonly fitted in a narrow binding energy regime of several eV using either a Shirley [1] or a Tougaard [2] background. We present an improved approach for XPS background fitting using reflective electron energy loss spectroscopy (REELS) data to calculate the inelastic electron scattering cross section (IESCS). As example the photoemission spectrum of aluminium was calculated in the binding energy range from 50 to 240 eV (Al 2s and 2p). We first fit the REELS spectrum considering the contribution of elastic scattered, directly excited surface plasmon, and inelastically scattered electrons. The results of this fit are then taken as starting parameters to fit the XPS spectrum. The fit results show a much better agreement with the measured spectrum as compared to those obtained with the conventional Tougaard background. Just as important, this method reveals the presence of several satellite peaks in the region of the plasmon peaks becoming apparent due to the simultaneous fitting of the detailed IESCS for the background calculation and XPS peak functions. This sensitivity to hidden satellite peaks can become a powerful tool to gain more knowledge from XPS spectra. [1] D. Shirley, Phys. Rev. B, Vol. 5, Nr. 12 [2] S. Tougaard, Solid State Commun., Vol. 69, Nr. 9

DS 21.12 Tue 12:30 CHE 91

Präparation verschiedener Substrate mittels anodischen Vakuum-Lichtbogens zum Aufwachsen von Graphen — •Konstantin Thronberens, Sebastian Schipporeit und Volker Buck — Arbeitsgruppe Dünnschichttechnologie, Fakultät für Physik, Universität Duisburg-Essen und CENIDE, 47057 Duisburg

Graphen ist einer der interessantesten Werkstoffe der jüngeren Geschichte. Seine einzigartigen Eigenschaften, sowohl in elektrotechnischer, optischer als auch in mechanischer Hinsicht, versprechen herausragende technische Anwendungsmöglichkeiten bei Verwendung von vergleichsweise günstigem Rohmaterial. Jedoch gestaltet sich die Herstellung von Graphen in großem Maßstab als schwierig, da beim epitaktischem Aufwachsen von Graphen auch leicht unerwünschtes Graphit gebildet werden kann. Eine mögliche Lösung des Problems stellt ein

Katalyseprozess dar. Als Katalysator für diesen Prozess können unter anderem Übergangsmetalle aus der Nickelgruppe wie Nickel, Platin und Palladium verwendet werden. Im Rahmen dieser Arbeit werden mit Nickel, Platin und Palladium beschichtete Saphirgläser hergestellt, die im Idealfall auch für die Verwendung als Substrat für das epitaktische Wachstum von Graphen geeignet sind. Für die Beschichtung der Saphirgläser wurde ein anodischer Vakuum-Lichtbogen verwendet, um kompakte Schichten mit einer hohen Haftung herzustellen.

DS 21.13 Tue 12:45 CHE 91

Investigation of molecular orientation in individual metal-organic nanowire by polarized Raman spectroscopy and simulation — •Yanlong Xing[1], Eugen Speiser[1], Dheeraj Singh[2], Petra Dittrich[3], and Norbert Esser[1] — [1]Leibniz-Institute for Analytical Sciences, ISAS Berlin, 12489 Berlin, Germany — [2]Department of Chemical Physics, Jacobs University, 28759 Bremen, Germany — [3]Department of Biosystems Science and Engineering, ETH Zurich, 8093 Zurich, Switzerland

To study the molecular self-organisation in metal-organic nanowires, single gold-tetrathiafulvalene (Au-TTF) nanowires were analysed using polarised Raman spectroscopy at room temperature. A first investigation was done for neutral tetrathiafulvalene (TTF) crystals. Based on the density functional theory calculation (DFT) of molecular Raman tensor and simulation of the depolarisation ratio, the orientation of TTF molecules in a single TTF crystal was revealed. The high correlation between results of the present work and that of reported single crystal data proved the efficiency of the proposed method in this work. Afterwards, both the experimental and simulation methods for TTF crystal was applied to study single Au-TTF nanowires. It was indicated that there were at least two different molecule configurations in the wire, both tilted with respected to the long axis of the wire. The 3D model of single Au-TTF wire shows a vivid image of molecular configurations in the wire. Compared to the proposed mechanism in previously reported work, this improved model can better explain the growth mechanism of Au-TTF wires with various morphologies.