DS 20: Focus Session: Emerging oxide semiconductors I (jointly with HL, DF, O)

Oxides are increasingly explored for their semiconducting properties. This session sets a focus to the physics, material and surface science of oxides that have recently been considered as active material for n-type and p-type semiconductor devices. Besides the classical use in gas sensorsand as transparent contactsfor optoelectronics devices, novel applications of semiconducting oxides in power electronics, UV sensors, photovoltaics, and solar water splitting devicesare addressed.

Organizers: Oliver Bierwagen, Paul-Drude-Institut für Festkörperelektronik, Berlin, Norber Esser, Leibniz-Institut für Analytische Wissenschaften ISAS, Berlin, Rüdiger Goldhahn, Otto von-Guericke-Universität Magdeburg, and Marius Grundmann, Universität Leipzig.

Time: Wednesday 9:30–13:00 Location: POT 081

Topical Talk DS 20.1 Wed 9:30 POT 081

Computational design of oxide semiconductors — •Stephan Lany — National Renewable Energy Lab, Golden, CO, 80401

Traditional semiconductors are the group-V, III-V, and II-VI systems as well as their isovalent and isostructural alloys. Within the field of oxide semiconductors, there is a continuing interest in n-type wide gap compounds, such as ZnO, In2O3 and related materials, but there is also growing interest in oxide semiconductors for novel applications, e.g., for oxide photovoltaics or solar water splitting. This background leads us to explore the range of possible semiconducting properties within the realm of oxide semiconductor alloys. From a computational materials design perspective, this includes modeling of the alloy structure and energetics, prediction of band-structures, optical properties, and electrical properties (doping and defects). We will discuss two recent examples of this materials design effort, i.e., the realization of tetrahedral MnO alloys, and the optimization of the photovoltaic properties of Cu2O by aliovalent alloying through ultrahigh doping.

Work in collaboration with H. Peng, V. Stevanovic, and funded by the U.S. Dept. of Energy.

DS 20.2 Wed 10:00 POT 081

Phonon properties of Copper-Oxide phases from first principles — •Marcel Giar, Markus Heinemann, and Christian Heiliger — I. Physikalisches Institut, Justus-Liebig-University, D-35392 Giessen, Germany

We present *ab initio* investigations on phonon properties of the copper-oxide phases Cu_2O, CuO, and Cu_4O_3. Phonon bandstructure and density of states for all three phases are derived from a supercell small displacement method. This method relies on displacing atom(s) within a supercell and calculating resulting forces on all other atoms. As copper-oxides exhibit polar bonding the splitting of the LO and TO modes at the Γ point must be properly taken into account. We derive these splittings from Born effective charges and the dielectric tensor which enter the non-analytical contributions to the dynamical matrix in the limit $\mathbf{q} \to 0$.

DS 20.3 Wed 10:15 POT 081

Intrinsic point defects in Cu_2O - Lifting of Raman selection rules — •Thomas Sander, Christian T. Reindl, and Peter J. Klar — I. Physikalisches Institut, Justus-Liebig-Universität Gießen

The copper oxide system Cu_2O receives currently a renewed interest due to its potential photovoltaic applications. Its natural p-type conductivity is due to intrinsic defects. Understanding the formation and properties of such point defects is of major relevance for tuning the material for optoelectronic applications.

Crystalline cubic Cu_2O exhibits a very unusual feature which is up to now unexplained in the literature. Instead of showing just one optical mode expected for cubic symmetry, Raman spectra of Cu_2O are dominated by Raman forbidden phonons independent of the method used for growth. A group theoretical analysis will be presented showing that the forbidden phonons will become Raman allowed when the symmetry is lowered due to the formation of point defects. Furthermore, it will be shown that of all possible intrinsic defects the copper split vacancies cause the lifting of the Raman selection rules. The results are experimentally confirmed by making use of the full angle and polarization dependence called rotational Raman spectroscopy (RoRa). Low temperature Raman studies further reveal that the degeneracy of phonon modes is lifted which is in accordance with the results of the group theoretical analysis.

Thus the detailed Raman study of Cu_2O in combination with the group theoretical analysis yields much more insight than just a proof of selection rules or identification of lattice modes.

DS 20.4 Wed 10:30 POT 081

Effect of Chemical Precursors On the Optical and Electrical Propertiesof p-Type Transparent Conducting Cr_2O_3:(Mg,N) — Elisabetta Arca, •Karsten Fleischer, Sergey A. Krasnikov, and Igor V. Shvets — School of Physics, Trinity College Dublin, Ireland

Cr_2O_3:(Mg,N) has been reported as a p-type transparent conducting oxide. In this contribution the effect of each precursor used for deposition by spray-pyrolysis will be explored and their role in determining the optical and electrical properties of Cr_2O_3 will be outlined. A correlation between the structural, electrical, and optical properties upon introducing nitrogen precursors has been established. In particular it has been shown that the presence of ammonium salts in the deposition environment results in less absorbing films. By combining optical measurements and NEXAFS studies, a mechanism is proposed to explain the change in the optical properties. Moreover, it is shown that the presence of the nitrate moiety in the reaction environment is necessary to improve the electrical conductivity of the deposited films. The reaction of the nitrate moiety with the ammonium moiety has been proposed as the mechanism to explain the boost in conductivity.

DS 20.5 Wed 10:45 POT 081

Tailoring the electronic and magnetic structure of doped rutile-TiO_2 using p-elements (C,N); A Hybrid DFT study. — •Jacqueline Atanelov, Christoph Gruber, and Peter Mohn — Vienna University of Technology, Center for Computational Materials Science

We study the electronic and magnetic structure of carbon and nitrogen impurities and interstitials in rutile TiO_2. To this end we perform *ab-initio* calculations of a 48-atom supercell employing the VASP code. In order to obtain a realistic description of the electronic and magnetic structure, exchange and correlation are treated with the HSE06 hybrid functional. Substitutional carbon and nitrogen are found to have a magnetic moment of 2 and $1\mu_B$, respectively, with a tendency for anti-ferromagnetic long range order. For C/N on interstitial sites we find that carbon is non-magnetic while nitrogen always possesses a magnetic moment of $1\mu_B$. We find that these interstitial positions are on a saddle point of the total energy. The stable configuration is reached when both carbon and nitrogen form a C-O and N-O dimer with a bond length close to the double bond for CO and NO. This result is in agreement with earlier experimental investigations detecting such N-O entities from XPS measurements. The frequencies of the symmetric streching mode are calculated for these dimers, which could provide a means for expermental verification. For all configurations investigated both C and N states are found inside the TiO_2 gap. These new electronic states are discussed with respect to tuning doped TiO_2 for the application in photocatalysis.

DS 20.6 Wed 11:00 POT 081

Magneto-optical characterization of thin films of magnetic oxides prepared via aqueous solution processing — •Peter Richter[1], Michael Fronk[1], Paul N. Plassmeyer[2], Catherine J. Page[2], Dietrich R.T. Zahn[1], and Georgeta Salvan[1] — [1]Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany — [2]Department of Chemistry, University of Oregon, Eugene, Oregon 97403, USA

Ferromagnetic oxides are of great interest for a wide variety of applications. In spintronics, LaMnO3 and La1-xSrxMnO3 are now among the most commonly used materials for electrodes. Other oxides like

the ferrites can show multiferroic properties and can be fabricated to be transparent and are therefore useful for optical and photovoltaic applications. However, the deposition of such magnetic oxide layers usually requires sophisticated instrumentation and may be expensive. We present a new approach to effectively prepare smooth thin films of metal oxides by spin coating them from aqueous precursor solutions. The full dielectric tensor (including the Voigt constant) of the obtained layers is determined from spectroscopic ellipsometry and magneto-optical Kerr effect (MOKE) spectroscopy measurements for a spectral range of 1.7 to 5.0 eV. The magnetic properties are investigated by MOKE magnetometry. Of particular interest, the ferrites $CoFe_2O_4$ and $NiFe_2O_4$ show characteristic spectral features and a ferromagnetic hysteresis at room temperature. We observe a variation of the optical and magnetic properties depending on the temperatures at which the samples were annealed after spin coating.

Coffee break (15 min.)

Topical Talk DS 20.7 Wed 11:30 POT 081

Beta-Ga2O3: Single crystal growth and semiconductor applications — •Encarnacion G. Villora[1], Daisuke Inomata[3], Stelian Arjoca[1,2], Kazuo Aoki[3], and Kiyoshi Shimamura[1,2] — [1]National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan — [2]Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 176-0022, Japan — [3]Koha Co., Ltd., Nerima, Tokyo 176-0022, Japan

β-Ga_2O_3 is a unique transparent conductive oxide, which is attracting an increasing attention in the recent years. It possesses two major features. The first is its very wide bandgap Eg=4.8 eV, which leads to a high transparency (>260 nm) and to a Baliga's figure of merit over three times that of GaN and SiC counterparts. The second feature is the capability to grow crystals from the melt, which makes possible the mass production of large substrates at low cost.

High quality 2 inch single crystals are grown by the EFG technique, and 4 inch are already in progress. N-type carrier concentration is controlled by Si- or Sn-doping. Conductive wafers are used as transparent conductive substrates for high-brightness vertically structured LEDs based on InGaN multi-quantum wells. Schottky barrier diodes and transistors have been demonstrated.

Additionally, a new phosphor concept for high-brightness white LEDs and LDs is presented. In contrast to currently used powder phosphors embedded in resins, single-crystal phosphors exhibit outstanding internal quantum efficiencies and do not degrade either under light irradiation or the increase of temperature.

DS 20.8 Wed 12:00 POT 081

MOCVD grown homo and heteroepitaxial β-Ga_2O_3 layer studied by transmission electron microscopy — •Robert Schewski, Martin Albrecht, Günter Wagner, Michele Baldini, Zbigniew Galazka, and Reinhard Uecker — Leibniz-Institut für Kristallzüchtung, Max-Born-Strasse 2, 12489 Berlin, Germany

We report on the structural properties of β-Ga_2O_3 layers, grown by MOCVD for various growth conditions. In detail, the influence of different precursors, namely pure oxygen, water, and CO_2 on the crystalline film quality has been investigated. Our studies were carried out for hetero- as well as homoepitaxially grown samples on (0001) sapphire and melt grown (100) β-Ga_2O_3 substrates, respectively. The conclusions are mainly based on transmission electron microscopy and x-ray data.

As main results, we found that pure oxygen in the growth ambient leads to the formation of nano-crystals in form of wires or agglomerates for both hetero- and homoepitaxial growth. However, by using water as oxygen precursor, smooth (rms: 6.5 nm) single crystalline layers can be achieved for homoepitaxial growth. Still, the structural quality of these thin films suffers from a substantial amount of stacking faults, which can be evidenced by TEM and x-ray data. However, annealing in oxidizing atmosphere at (900°C) leads to a reduction these stacking faults and thus improves the crystalline quality of the film. Another interesting observation is the formation of a pseudomorphic, 3 monolayers thick Ga_2O_3 layer in the alpha phase, directly at the interface between the sapphire substrate and the film.

Topical Talk DS 20.9 Wed 12:15 POT 081

Combinatorial approach to group-III sesquioxides — •Holger von Wenckstern — Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik II, Halbleiterphysik

Semiconducting group-III sesquioxides find potential application as chemical/biological sensors, deep-UV photo-detectors, and within transparent and high-power electronics. Technology for bulk growth of binary Me_2O_3 (Me=Al, Ga, In) exists and first promising devices on homoepitaxial layers have been demonstrated. For the exploration of ternary or quarternary systems thin film technology is required. In this contribution we introduce a facile approach to create lateral continuous composition spread(s) (CCS) within thin films on 2 inch wafers by pulsed-laser deposition (PLD) [1]. We ablate from a single, segmented, rotating target keeping the growth rate is for this approach as high as for conventional PLD. We will illustrate the potential of our CCS-technique and discuss structural, optical and electronic properties of $(In,Ga,Al)_2O_3$ thin films and their utilization in device demonstrations like rectifiers or photo-detectors.

[1] H. von Wenckstern *et al.*, CrystEngComm **15**, 10020 (2013)

DS 20.10 Wed 12:45 POT 081

Schottky contacts on β-Ga_2O_3 and In_2O_3 thin films — •Daniel Splith[1], Stefan Müller[1], Holger von Wenckstern[1], Oliver Bierwagen[2,3], James S. Speck[3], and Marius Grundmann[1] — [1]Universität Leipzig, Institut für Experimentelle Physik II, Leipzig, Germany — [2]Paul Drude Institut, Berlin, Germany — [3]Materials Department, University of California, Santa Barbara, USA

Oxide semiconductors like β-Ga_2O_3 or In_2O_3 are promising materials for a new generation of transparent electronic devices. Oxide field-effect transistors but also the electrical characterization of these oxides by capacitance-voltage measurements or deep-level transient spectroscopy rely on Schottky contacts (SCs). For our study we fabricated SCs on β-Ga_2O_3 and In_2O_3 thin films and investigated their electrical properties. The β-Ga_2O_3 thin films were grown by pulsed laser deposition on highly conducting (00.1) oriented ZnO:Ga acting as a back contact layer. The In_2O_3 thin films were grown by molecular beam epitaxy on yttria-stabilized zirconia substrates. We prepared SCs by dc sputtering of different metals. On β-Ga_2O_3 the I-V characteristics of Cu SCs exhibit high rectification ratios up to 7 orders of magnitude. Temperature dependent measurements between 110 and 320 K yield a mean barrier height of 1.32 eV, which is in accordance to the effective barrier height at a temperature of 550 K, where the ideality factor decreases to 1.03. Due to surface electron accumulation, the realization of SCs on In_2O_3 is challenging. In a proof of principle experiment we fabricated SCs on In_2O_3 by reactive sputtering of Au, Pt and Pd with rectification ratios up to 3 orders of magnitude.