Monday Afternoon, October 29, 2012

Actinides and Rare Earths Focus Topic
Room: 6 - Session AC+TF+SS+MI-MoA

Actinides and Rare Earths: Thin Films and Surface Science
Moderator: R.K. Schulze, Los Alamos National Laboratory

2:00pm **AC+TF+SS+MI-MoA1 Rare Earth 4*f* Hybridization in Gallium Nitride**, *J.W. McClory*, *S.R. McHale*, Air Force Institute of Technology, *L. Wang, W.N. Mei*, University of Nebraska-Lincoln, *J.C. Petrosky*, Air Force Institute of Technology, *J. Wu, R. Palai*, University of Puerto Rico – San Juan, *Ya.B. Losovyj*, Louisiana State University, *P.A. Dowben*, University of Nebraska-Lincoln **INVITED**
The location of the Gd, Er and Yb 4*f* states within the GaN valence band has been explored both experimentally and theoretically. The $4d - 4f$ photoemission resonances for various rare earth doped GaN thin films (RE = Gd, Er, Yb) provide an accurate depiction of the occupied 4*f* state placement within the GaN valence band. The resonant photoemission show that the major Er and Gd rare earth 4*f* weight is at about 5-6 eV below the valence band maximum, similar to the 4*f* weights in the valence band of many other rare earth doped semiconductors. For Yb, there is very little resonant enhancement of the valence band of Yb doped GaN, consistent with a largely $4f^{14-d}$ occupancy. The placement of the rare earth 4*f* levels is in qualitative agreement with theoretical expectations.

2:40pm **AC+TF+SS+MI-MoA3 Revisiting the Yb Electronic Structure with Low-Energy Photoemission Spetroscopy**, *F. Offi*, CNISM and Univ. Roma Tre, Italy, *P. Vilmercati, L. Petaccia, S. Gorovikov*, ELETTRA Sincrotrone Trieste, Italy, *A. Ruocco*, CNISM and Univ. Roma Tre, Italy, *M.I. Trioni*, CNR-ISTM, Milano, Italy, *A. Rizzo*, CNISM and Univ. Roma Tre, Italy, *A. Goldoni*, ELETTRA Sincrotrone Trieste, Italy, *G. Stefani*, CNISM and Univ. Roma Tre, Italy, *G. Panaccione*, CNR-IOM, Basovizza-Trieste, Italy, *S. Iacobucci*, CNI-IFN, Rome, Italy
The peculiar electronic structure of rare-earth elements and compounds is mostly defined by the partially filled 4*f* band. Of particular interest is the investigation of the valence states, which is linked to the degree of hybridization of *f* electrons with delocalized *s-d* bands. In the simple case of Yb, the 4*f* states are fully occupied with a Fermi level of 6*s* character and a 2+ valency. However, the occupation of the Yb valence band has been the subject of several investigations over the years, intended in particular to separate the contribution of 5*d* states. Early experimental photoelectron emission (PES) spectra at very low excitation energy ($hv < 10$ eV) have reported a spectral modulation in the region close to the Fermi level that was attributed to the emission from a 5*d* band. The poor energy resolution did not allow however a detailed investigation of such spectral features. In recent years this low energy photoemission spectroscopy (LEPES) encountered a renewed interest, under the stimulus of the extremely high energy resolution obtainable with laser excited LEPES and given the expectation of a large increase of the bulk sensitivity at these low energies. W e monitored the 4*f* spectral intensity in polycrystalline Yb films in the LEPES regime (between 5.5 and 21 eV photon energy, with experiments at the BaDELPH beamline of the ELETTRA synchrotron radiation facility), observing a moderate increase of the electron attenuation length and, thus, a moderate increase of the information depth when we reach the lowest energies. By lowering the photon energy below about 11 eV a prominent peak at the Fermi level is observed. The analysis of its intensity variation versus photon energy and the comparison of the experimental spectra with *ab initio* density of states (DOS) calculations allow to attribute this structure to a *p* band crossing the Fermi level, enhanced at selected photon energies due to the influence of the empty DOS, probably amplified by a photoionization cross section effect and by the general increase of the photoelectron yield at low photon energy. In this respect LEPES may thus be considered as a probe of the joint DOS.

3:00pm **AC+TF+SS+MI-MoA4 Erbium Rare Earth Thin Film Hydride Stress Studies as a Function of Processing Techniques**, *J.L. Provo*, J.L. Provo Consulting
An important part of understanding the behavior of rare earth, Group 3A and 4A thin film hydrides is the determination of indirect effects such as stress in the film lattice which can lead to film flaking. In this study, special vacuum sample containers were prepared to observe and record basal-plane film stress levels, and film flaking (optical observations).

The special vacuum sample containers contained erbium deuteride (ErD_2) and erbium tritide (ErT_2) films on AT and BT quartz resonator substrates with chromium underlays in pairs prepared by air-exposure, (in-situ) evaporate-load and reactive evaporation hydriding techniques. The erbium deuteride samples were prepared as controls for aging studies. All samples were processed with PVD Electron Beam deposition techniques, hydriding techniques mentioned above and a 450°C temperature bakeout and exhaust in consideration of the α→β crystal phase transformation in crystalline quartz at 573°C.

Samples for the measurement of initial film deposition stress as a function of hydride processing and for the determination of stress produced in ErT_2 films due to the generation of helium-3 with time (i.e., tritium decay) were designed to utilize the double- resonator technique developed by EerNisse(1). Measurements of mass change and induced film stress were determined by frequency measurement changes obtained with a precision frequency counter, data being taken from the output of a one transistor Colpitts type driving oscillator circuit in which the crystal is an integral part.

A summary of initial film deposition stress (tensile) and film aging accumulative stress (compressive) for the erbium films from the different deposition and hydriding techniques is given. Reactively evaporated erbium occluder films were seen to have an initial film deposition tensile stress approximately 5 times less than (in-situ) evaporate-load films and 11 times less than air-exposed loaded films. Acculumative aging compressive stress for erbium occluder films were shown to be more variable but data indicate that reactively evaporated film aging stress is less than that of (in-situ) evaporate-load and air –exposed tritided films.

(1)-J. Appl. Phys. 43, 1330 (1972)

3:40pm **AC+TF+SS+MI-MoA6 Splat Cooling Technique Contributing to Understanding of Uranium Systems**, *L. Havela*, Charles University, Czech Republic, *A. Gonçalves, J.-C. Waerenbogh, L. Pereira*, ITN Sacavém, Portugal, *I. Tkach*, Charles University, Czech Republic, *N.-T. Kim-Ngan*, Pedagogical University Cracow, Poland, *T.B. Scott*, University of Bristol, UK
The splat cooling technique is one of the methods of ultrafast cooling of a melt, particularly suitable for small amounts of material. In particular cases it can help to overcome constraints imposed by thermodynamics. One of them was the issue of magnetic properties of non-stoichiometric Laves phase UFe_2. This compound has a ferromagnetic ground state (with both U and Fe magnetic moments). An excess of U, achieved by quenching, led to the decrease of T_C from 162 K for pure compound to 112 K for $UFe_{1.7}$ [1]. Quenching was, however, unable to provide Fe-rich material, with expected increase of T_C. Using splat cooling of a series of materials with various off-stoichiometry from UFe_2 to UFe_6 we found that the cubic Laves phase structure (with sum-micron grains) can absorb excessive Fe up to the stoichiometry $UFe_{2.3}$. Additional excess leds to the segregation of α-Fe [2]. The increase of TC up to 230-240 K was the impact on magnetic properties. The spontaneous magnetization also increases from 1.0 μ_B/f.u. in UFe_2 to 1.9 μ_B/f.u. in $UFe_{2.3}$. ^{57}Fe Mössbauer spectroscopy reveals that the excessive Fe atoms enter the U sublattice and develop higher magnetic moments (approx. 1.0 μ_B/Fe).

Applying the splat cooling technique on pure and doped U metal had the aim to stabilize the high temperature *bcc* phase (γ-U) to low temperatures, to be able to establish its basic electronic properties. In particular, changes in magnetic characteristics and electronic specific heat can be expected due to the modest volume expansion comparing to orthorhombic α-U. We found that splat cooling reduces the necessary concentration of dopants and U with 12 at.% Mo has no traces of α-U. The Sommerfeld coefficient $\gamma = 19$ mJ/mol K^2 estimated for pure γ-U is enhanced comparing to 11 mJ/mol K^2 for pure U splat, which is close to values given in literature [3] for the U metal. The splats exhibit a superconducting ground state with T_c ranging from 1.24 K for pure U to 2.11 K for 15 % Mo. The γ-U superconductivity is characterized by a large critical field exceeding 6 T and a sharp λ-type anomaly in specific heat $C_p(T)$ with the size corresponding to the BCS theory. The superconductivity of a pure U splat, which contains only traces of γ-U, has much lower critical field (0.33 T) and the weak anomaly in $C_p(T)$ does not convince about the bulk character of superconductivity.

[1] A.T. Aldred, J.Magn.Magn.Mater. 10, 42 (1979).

[2] L. Havela et al., Intermetallics 19, 113 (2011).

[3] J.C. Lashley et al., Phys. Rev. B 63, 224510 (2001).

4:00pm AC+TF+SS+MI-MoA7 Investigation of Rare Earth Doped Lithium Tetraborate Glasses with XAFS and Emission and Excitation Spectroscopy, *T.D. Kelly, J.W. McClory, D.A. Buchanan, A.T. Brant, J.C. Petrosky,* Air Force Institute of Technology, *Ya.B. Losovyj,* Louisiana State University, *V.T. Adamiv, Ya.V. Burak,* Institute of Physical Optics, *P.A. Dowben,* University of Nebraska-Lincoln

The local structure of rare earth doped lithium tetraborate ($Li_2B_4O_7$) glasses has been studied by extended x ray absorption fine structure (EXAFS) at the rare earth L shells and by optical emission and excitation spectroscopies. The samples investigated were 1% rare earth doped by weight with Gd and Nd. The EXAFS signal was recorded in fluorescence mode with the energies calibrated for Nd L1 and L3 edges and Gd L3 edge. X rays were applied to the samples to activate emission and excitation centers in the glasses. The spectra were analyzed to determine rare earth occupation sites in the lithium tetraborate crystal structure and the emission and excitation lines due to rare earth doping.

4:40pm AC+TF+SS+MI-MoA9 Eu-implanted p-type GaN: Charge-Driven Luminescence Hysteresis and Identification of a Possible Charge-State-Alternation Resonance of the Mg Acceptor, *K.P. O'Donnell, P.R. Edwards, R.W. Martin,* Strathclyde University, Scotland, UK, *K. Lorenz, E. Alves, V. Darakchieva,* ITN Sacavém, Portugal, *M. Bockowski,* Unipress, Poland

Europium-doped p-type GaN shows *spectral switching* and *luminescence hysteresis* when samples are temperature-cycled between room temperature and 20 K (*K.P. O'Donnell et al, Late News paper at ICPS2012, Zurich*). An explanation of this unusual behaviour may be found in the charge-state dependence of the local structure of the Mg acceptor in GaN, recently modelled by J.L. Lyons et al., (Phys. Rev. Lett. 108, 156403 (2012)). Eu ions, sensitive to their local environment, may act as 'spectators' of the charge-induced local distortions. The dominant impurity-induced luminescence spectrum at RT (hereafter, Eu0) *switches completely* to another spectrum (Eu1) when samples are cooled below 25 K. Upon subsequent warming of the sample, Eu1 fades with increasing temperature, as expected, but Eu0 *does not reappear* until the temperature exceeds 150 K; its recovery is complete only above 210 K. The noted temperature extremes correspond to hole localisation (carrier freeze-out) and delocalisation, respectively. Here, we extend Lyons' model to consider the possibility of observing the resonance in which the acceptor alternates rapidly between neutral and negative charge states, leading to a spatial oscillation of the associated defect between Eu0 and Eu1 forms, and describe the possible spectral identification of this resonance.

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