

1st FunMAX WORKSHOP 2020

An international ONLINE workshop on the properties
of Functional MAX Materials



August 10 - 12, 2020



Kirensky Institute of Physics
Krasnoyarsk, Russia

The first FunMAX workshop aims at bringing together scientists from different areas in materials science interested in the physical properties of MAX phases (nano-laminated structures consisting of layers of d-elements (M), group IV elements (A) and carbon or nitrogen or boron (X)).

We kindly invite experimental and theoretical research contributions related to functional fundamental phenomena as well as design, properties and applications of MAX and MX materials.

The 1st FunMAX 2020 workshop will include a maximum of 20 oral presentations (Invited, contributed and tutorial) and plenty of time for online discussions.

Book of Abstracts

Tutorials	page 1 – 2
Invited	page 3 – 14
Contributed	page 15 -22

Organizers: Michael Farle, Anton Tarasov, Sergei Ovchinnikov

Secretary: Tatyana Smolyarova

Tutorial:

Spin-Polarized Scanning Tunneling Microscopy and Spectroscopy of Single Hybrid Molecular Magnets

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I will discuss the nanomagnetic characterization of individual hybrid molecular magnets by exploiting the topographic, electronic, and magnetic imaging and measuring capabilities of spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/STS) [1].

Hybrid molecular magnets are formed upon chemisorbing aromatic molecules on ferromagnetic transition-metal surfaces. The hybridization between the molecular π -orbitals and the spin-split d -states of the substrate results in a spin-imbalanced molecular density of states (DOS). As a consequence, the chemisorbed molecule exhibits, depending on the molecule-substrate interaction strength, an induced magnetic moment and spin polarization (SP) near the Fermi level or a spin-dependent HOMO-LUMO gap [2]. The substrate atoms that are bound to the molecule are also electronically and magnetically modified. Their mutual in-plane exchange coupling is enhanced, whereas the exchange coupling to the surrounding substrate atoms in the uppermost layer and to those in the second uppermost layer is reduced. Therefore, the chemisorbed molecule together with the substrate atoms bound to it can be considered as a new magnetic unit, a so-called hybrid molecular magnet, with enhanced coercivity and Curie temperature [3].

In order to study the nanomagnetic properties of such single-molecule hybrids, we deposit in ultra-high vacuum sub-monolayer amounts of suitable aromatic molecules by sublimation onto pre-cleaned, single-crystalline transition-metal surfaces. STM topography images yield detailed information about the integrity of the molecule after adsorption, the adsorption geometry on the substrate lattice, and also intramolecular orbital resolution on the sub-nm scale. This structural information is required for setting up an atomistic model as input for spin-resolved density-functional theory (DFT) calculations. STS measurements (recording tunneling current I while sweeping the bias voltage V for vertically and laterally fixed tip position) yield conductivity (dI/dV) curves that represent to a good approximation the local DOS of the sample. dI/dV -maps measured at a fixed bias voltage V_0 while scanning the tip show laterally resolved intensity variations of DOS features at the energy $E_{\text{Fermi}} + V_0$, allowing imaging of molecular orbitals with intramolecular resolution. Using spin-polarized (e.g. ferromagnetic) tips adds magnetic sensitivity due to the magnetoresistance effect between tip and sample. Differences between topography or conductivity data obtained for parallel and antiparallel alignment of tip and sample magnetizations can be related to the local SP of the sample, enabling the measurement of spatially and energetically resolved SP-maps on the sub-nm scale.

I will present exemplary data for triphenyl-triazine molecules adsorbed on 2 ML Fe/W(110) [4] and Co bilayer nano-islands on Cu(111) [5] as well as for an especially designed and synthesized cyclophane based on pyrene and ferrocene that exhibits a unique ecliptic aromatic plane arrangement and is also adsorbed on Co bilayer nano-islands on Cu(111) [6].

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Tutorial: Ferromagnetic Resonance: Theory and Applications for thin magnetic films

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Ferromagnetic resonance (FMR) is a spectroscopy technique for an in-depth investigation of the magnetic properties of nanomaterials. It is based on the detection of magnetization precession via the measurement of microwave absorption (usually in GHz range) as a function of external field/frequency [1]. The resonance conditions in ferromagnetic materials are determined by the contributions of shape anisotropy (defined by the demagnetizing factor), magnetocrystalline anisotropy, strength and direction of the applied DC magnetic field in combination with a frequency of RF microwaves. Thus, FMR spectroscopy is a primary tool for analysis of magnetic anisotropy contributions and g-factors of magnetic materials. The frequency-dependent spectrum linewidth provides an information about relaxation processes in ferromagnets and Gilbert damping. For thin ferromagnetic films and multilayers, FMR spectroscopy is a world-known technique for studying the variation of magnetic anisotropy [2,3,4], Gilbert damping [5,6], spin-pumping effects [7-9] and magnetic phase transitions [2,8,9].

In the tutorial, the theoretical background of FMR will be introduced with the focus of Smit-Beljers approach, and the common measurement techniques will be overviewed. The FMR studies will be illustrated with examples of thin magnetic films of nanolaminated MAX phases [2,3,10].

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INVITED Presentations

(alphabetical order with last name)

Creative synthesis techniques to access “old and new” MAX phases

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Ternary transition metal-based carbides and nitrides that belong to the family of MAX phases are chemically versatile layered solids with a unique set of properties.¹ While more than 80 members, and far more if solid-solutions are taken into account, have been prepared so far, their compositional space is far from being depleted. Many new phases, that have not been experimentally realized yet, are expected to exist and are exciting functional materials to be explored. Furthermore, especially carbonitride and nitride MAX phases will unlock the path to new two-dimensional MXenes.

Typically, MAX phases are prepared by high-temperature solid-state methods. While these are powerful techniques, they might not be sufficient to explore the full compositional space of these ternary/quaternary systems. Our group uses creative synthesis techniques based on wet chemical and non-conventional solid-state syntheses to access the target MAX phases. This has, for example, led to V₄AlC₃ that had only been prepared in the form of carbon-deficient single crystals and as a minor side phase in polycrystalline VC prior to our work.² Beside granting access to new or underexplored MAX phases, the wet chemical-based methods expand the microstructural space of bulk MAX phases and lead, for example, to anisotropic particles.³

In this talk, I will show some examples of MAX phases that have been prepared by microwave heating, a newly-developed sol-gel-based method as well as our recent reactions in liquid ammonia. The latter is particularly exciting as it allows for synthesis of nitride MAX phases. The discussed Cr- and V-based MAX phases are mainly characterized by X-ray diffraction and electron microscopy.

Acknowledgement

We acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 405553726 – TRR 270.

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Anisotropic conductivity in thin films of MAX phase $(\text{Mn}_{0.5}\text{Cr}_{0.5})_2\text{GaC}$ and crystallites of i-MAX phase $(\text{Cr}_{2/3}\text{Ho}_{1/3})_2\text{AlC}$

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A novel direct and parameter-free method is presented for the accurate determination of the perpendicular-to-plane resistivity and resistivity anisotropy of a thin-film sample without any further sample treatment [1]. A multi-probe scanning tunneling microscope is used to carry out 4-probe transport measurements with variable probe configurations. The observation of the crossover from the 3D electronic transport regime for small spacings between probes to the 2D regime for large spacings enables the determination of both in-plane and perpendicular-to-plane resistivities ρ_{ab} and ρ_c . If the probes are arranged in a square configuration, in-plane resistivities ρ_a and ρ_b can be obtained by rotating the square configuration with respect to the sample [2].

Applying the method of varying probe spacings to a $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ MAX phase thin film yields a large perpendicular-to-plane anisotropy ratio $\rho_c/\rho_{ab} = 525 \pm 49$ and low in-plane resistivity $\rho_{ab} = (1.14 \pm 0.04) \mu\Omega\text{m}$ [1]. This is a consequence of the complex bonding scheme of MAX phases with covalent M–X and metallic M–M bonds in the MX planes and predominately covalent, but weaker bonds between the MX and A planes [3-5]. Combining both methods by first rotating the square probe configuration and then varying the probe spacing (edge length of the square) at a fixed square orientation to crystallites of orthorhombic $(\text{Cr}_{2/3}\text{Ho}_{1/3})_2\text{AlC}$, which belongs to the i-MAX phases with in-plane chemical ordering [6,7], yields clear evidence for both in-plane ($\rho_a/\rho_b \approx 1.5$) and perpendicular-to-plane (4...40) resistivity anisotropy. The in-plane anisotropy is a consequence of the chemical ordering of the transition and rare-earth atoms. The weaker perpendicular-to-plane anisotropy compared to conventional MAX phases corroborates predictions of less anisotropic band structures for i-MAX phases [6]. These measurements represent the first characterization of anisotropic resistivity in an i-MAX phase and furthermore give proof-of-principle for the determination of the entire resistivity tensor of a material with orthorhombic or higher symmetry through 4-probe electronic transport measurements of a single thin or crystalline sample.

Acknowledgement

J.R. acknowledges support from the Knut and Alice Wallenberg (KAW) Foundation for a Fellowship Grant as well as from the Swedish Research Council through Project No. 642-2013-8020.

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Prediction of order and disorder in MAX phases

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The exploration of MAX phases can be accelerated by theoretical structural design on the atomic level combined with combinatorial experimental synthesis. This was recently demonstrated for a range of MAX phase alloys, (i) *o*-MAX with out-of-plane chemical order and (ii) *i*-MAX with in-plane chemical order (1-6). We use predictive phase stability calculations to explore MAX phases upon alloying between two transition metals, M' and M'' , from Group 3 to 9. The materials investigated focus on *o*-MAX and *i*-MAX phases with and their disordered counterparts. We confirm all experimentally known phases to date, and suggest a range of stable ordered and disordered hypothetical combinations. We also suggest rules for when preference for chemical order or disorder are expected. In extension, we suggest a matching set of novel MXenes, from selective etching of the A-element. The here demonstrated structural design on atomic level expands the property tuning potential of functional ceramics.

Acknowledgement

Swedish Research council and the Swedish National Infrastructure for Computing (SNIC)

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Element-specific and spatially-resolved detection of the magnetization
and its dynamics by X-ray Magnetic Circular Dichroism (XMCD)

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For future magnonic [1] and spintronic [2] devices, which are possible applications for magnetic MAX phases [3], the element-specific and spatially-resolved investigation of the magnetization and its dynamics in the GHz regime is an essential requirement. X-ray Magnetic Circular Dichroism (XMCD) allows to extract information on the orientation and the size of magnetic moments with unidirectional alignment [4]. The sample is element specifically probed using circularly polarized X-rays with a photon energy set to an X-ray absorption edge of the investigated material with parallel or antiparallel helicity with respect to the orientation of the magnetic moments. By employing magneto-optical sum rules the orbital- and spin portion of the magnetic moment can be extracted from XMCD data [4]. With Scanning Transmission X-ray Microscopy (STXM), XMCD can be spatially-resolved measured with a resolution down to 10 nm [5]. Magnetization dynamics can be probed by XMCD with X-ray detected (Ferro)-Magnetic Resonance (XDMR/XFMR) [6]. By using a Scanning Transmission X-ray Microscope (STXM-FMR) it is possible to map (spatial resolution < 50 nm) dynamic excitations of the magnetization up to 10 GHz with ps sampling [7].

The talk will give an introduction to the physical background of the XMCD effect and to the sum rules. In addition, an overview on the STXM-FMR technique will be given illustrated by the visualization of the resonant response at 6.748 GHz of a single Fe₃O₄ nanoparticle chain (19 particles with a single particle size of 40 nm to 50 nm) grown by biomineralization in a magnetotactic bacterium. The nanoparticle chains in such bacteria are suggested to be employed for biomagnonic logic devices by manipulating the magnon dispersion of such chains with the DNA controlled arrangement of the particles [8]. The presented results are supplemented by micromagnetic simulations which show a good agreement to the experiment.

Acknowledgement

Research performed in collaboration with R. Meckenstock, D. Spoddig, B. Zingsem, H. Ohldag H. Wende, M. Farle, M. Winklhofer and K. Ollefs. Financial support: FWF Project No. I-3050, ORD-49 and DFG Project No. 321560838.

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Spectral magneto-ellipsometry of epitaxial Mn₂GaC MAX phase

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Some time ago a new magnetic MAX material in the form of a heteroepitaxial thin film Mn₂GaC on a MgO(111) substrate was theoretically predicted and later synthesized [1]. The synthesized structure is an excellent model system for studying complex magnetic phenomena occurring in atomic-layered materials [2]. Previous studies of the structure of Mn₂GaC/MgO(111) [3] showed that the Neel temperature in Mn₂GaC is about 507 K. When cooled below 214 K, antiferromagnetic Mn₂GaC undergoes phase transition of the first order from collinear to non-collinear spin state. Both states demonstrate a large uniaxial magnetostriction perpendicular to the Mn-C-Mn layers, which is a result of the magneto-structural transformation into a ferromagnetic configuration induced by a strong magnetic field. According to magnetometry data, the sample Mn₂GaC/MgO(111) has a residual magnetization at room temperature in low fields.

The detected existence of non-equivalent states of Mn and Ga ions in the Mn₂GaC unit cell can influence electronic and magnetic properties and, consequently, can be detected in the spectra of optical absorption and magnetic circular dichroism (MCD) [4]. Thus, it is possible to obtain information about the type of ions involved in the ferrimagnetic ordering in low fields at high temperatures from the temperature changes of MCD spectra.

We measured the full dielectric permeability tensor, optical absorption and MCD spectra of Mn₂GaC epitaxial film at 140 and 296 K using spectral magneto-ellipsometry in fields up to 200 mT along with Mn-C-Mn layers. The transition at 214 K is characterized by changes in the crystal structure across the Mn-C-Mn layers resulting in significant changes in optical absorption peaks when cooled from 296 to 140 K. Temperature changes of peaks in MCD and optical conductivity spectra indicate the influence of transitions between Mn ions and transitions between Mn – Ga. In turn, uncompensated magnetic moments between alternating layers of Mn-C-Mn lead to ferrimagnetic properties of the sample at room temperature. According to the field dependencies of the Kerr magneto-optical effect, the hysteresis loop shifts on the film surface by a value inversely proportional to the temperature, indicating a possible contribution of the Mn₂GaC surface to the bulk magnetic properties of the sample.

Acknowledgement

The research was supported by the government of the Russian Federation (agreement No. 075-15-2019-1886)

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A variety of ways to determine doping concentration by X-ray diffraction

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Nowadays the doping of host material is one of the main ways to distort/change the host material and the concentration level is an important parameter which should be estimated. Usually the X-ray diffraction is used to make this analysis. However sometimes the ion radii of doped ions are close to the ion radii of replaced ion and structural deformation is subtle. In this case the task of simple proving/disproving doping of the host material becomes very complex. The task of doped site localization seems to be impossible (Figure 1).

This presentation will show three ways how to solve this problem. Each suggested method imposes the restrictions for the maximal values of estimated standard deviation (esd) of structural parameters (ΔV , Δocc or Δx) which should be obtained after the Rietveld refinement. Obviously their values depend on the quality of X-ray data and sometimes demand some special experimental conditions. Fortunately the required ΔV , Δocc or Δx can be estimated before any experiments and before Rietveld refinement process. The information about rough structural model of the host and the information about doped/replaced ions is needed only. In current presentation several examples will be shown.

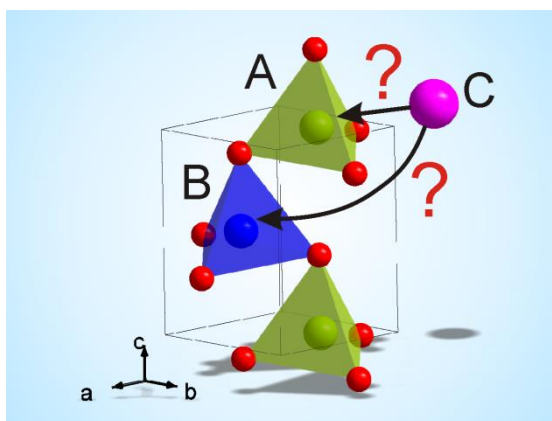


Figure 1. Two possible mechanism of doping host material and the most probable one can be determined using X-ray diffraction

Temperature and concentration dependence of the magnetic short range order and electronic pseudogap in 2D Hubbard model

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Magnetic MAX materials has quasi-two-dimensional magnetic and electronic properties. There are several other quasi-two-dimensional magnetic materials, the most studied are high-temperature cuprates with a peculiar properties of the doped CuO₂ layers. In this talk the review of the short range antiferromagnetic order, its doping and temperature dependence and its effect of formation of the superconducting state and unusual pseudogap state will be given. Strong temperature and doping dependencies of the electronic structure of cuprates are well established now by combination of many methods, especially ARPES. These dependencies can not be described by any versions of the DFT theory. Due to strong electron correlations responsible for the formation the main electronic and magnetic properties of cuprates we use our original multielectron version of the tight-binding approach (GTB), with model parameters calculated by ab initio approach (LDA+GTB) [1]. Short range antiferromagnetic correlations determine the electronic self-energy and have been calculated self-consistently for different doping [2], that results in two Lifshitz quantum phase transitions with doping. The first one determines the optimal doping and maximal superconducting critical temperature T_c, the second transition is related to the pseudogap-normal Fermi liquid transition. This picture was obtained in static approximation for spin correlations, and the calculated Fermi surface did not reproduce the ARPES data. Recently we have studied the evolution of the Fermi surface and normal state properties within more elaborated cluster perturbation theory that includes all correlations inside the 4x4 cluster exactly with perturbative treatment of the intercluster interactions [3]. This approach demonstrates two smooth crossovers from strong pseudogap regime to weak pseudogap one and further in the normal Fermi liquid state both with increasing doping and temperature. This evolution is accompanied with the changes of the short range magnetic correlations and is in a qualitative agreement to the ARPES experimental data [4].

Acknowledgement

We acknowledge the Russian Academy of Science Program on High_T_c superconductivity for the financial support.

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Ion Implantation: A New Approach for Structural Modification of Two-Dimension MXenes

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Ion implantation is among the most versatile approach to modify, in a controlled way and with possible access to out-of-equilibrium states, the structure and physical properties of solids. In that sense, it has been widely used in the semiconductor industry for doping or engineering electronic devices.

In this study, we employed the potentiality of ion implantation in respect to 2D MXenes and demonstrate the controllable structural induced modification. The direct impact of low-energy ion implantation of Mn-ions into $Ti_3C_2T_x$ MXene structure has been assessed with thorough experimental characterizations such as SEM/EDS, XPS, ToF-SIMS and with electron energy loss spectroscopy analyses (EELS). With the help of ToF-SIMS and SEM/EDS, we experimentally confirm successful Mn doping into $Ti_3C_2T_x$ thin film with a maximum content of 2.2 at.%. Analyzing the structural evolution of Mn-implanted $Ti_3C_2T_x$ film, we point out that ion implantation causes strong chemical modification of MXenes, resulting in defects formation in both Ti and C sites. By using EELS/TEM we demonstrate that produced defects offer new crystallographic sites extremely favorable for the oxygen functionalization with a dramatic increase of the O content with respect to pristine films. Despite the structural damages due to the ion implantation and induced increase of O content, the MXene are still metallic.

Explored structural modification of $Ti_3C_2T_x$ MXene induced by ion-implantation in this study open new and not yet explored possibilities to master, in a simple way, the properties of 2D MXenes by tuning ion species and dopant concentration.

Growth of α -FeSi₂ nanocrystals on silicon surface: the impact of gold and the Si/Fe flux ratio, the origin and the prediction of α /Si orientation relationships and interface structures

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A pure crystallogeometrical approach is proposed for predicting orientation relationships, habit planes and atomic structures of the interfaces between phases, which is applicable to systems of low-symmetry phases and epitaxial thin film growth [1]. The suggested models are verified with the example of epitaxial growth of α -, γ -, and β -FeSi₂ silicide thin films and nanocrystals on silicon substrates on silicon substrates. The growth of α -FeSi₂ nanocrystal ensembles on gold-activated and gold-free Si(001) and Si(111) surface under different Si/Fe flux ratio by molecular beam epitaxy is reported. The study reveals the utilisation of gold as a catalyst regulates the preferable orientation relationship (OR) of the nanocrystals to silicon and their morphology at given Si/Fe flux ratio [2]. The density of near-coincidence sites is shown to have a decisive role in the determination of epitaxial α -FeSi₂ nanocrystal orientation and explains the formation of α /Si interfaces. The density of near-coincidence sites is shown to have a decisive role in the determination of epitaxial thin film orientation and explains the superior quality of β -FeSi₂ thin grown on Si(111) over Si(001) substrates despite larger lattice misfits. Ideal conjunctions for interfaces between the silicide phases are predicted and this allows for utilisation of thin buffer α -FeSi₂ layer for oriented growth of β -FeSi₂ nanostructures on Si(001). The thermal expansion coefficients are obtained within quasi-harmonic approximation from the DFT calculations to study the influence of the temperature on the lattice strains in the derived interfaces. Faster decrease of misfits at α -FeSi₂(001)||Si(001) interface compared to γ -FeSi₂(001)||Si(001) elucidates the origins of temperature-driven change of the phase growing on silicon substrates. The proposed prediction approach guides from bulk phase unit cells to the construction of the interface atomic structures and appears to be a powerful tool for the prediction of interfaces between arbitrary phases for subsequent theoretical investigation and epitaxial film synthesis.

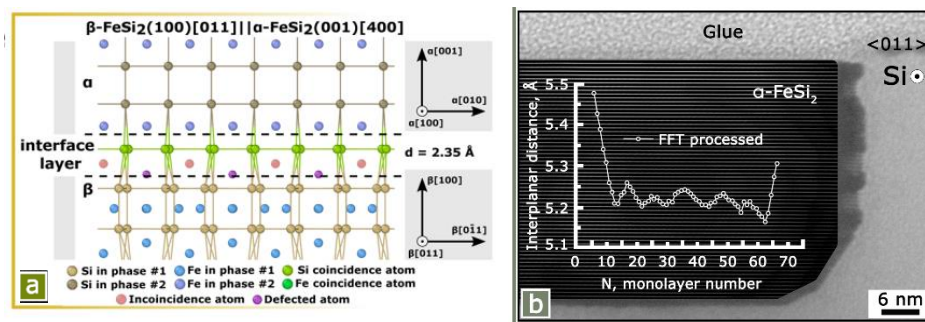


Figure 1. An example of automatically created atomic structure model for an interface between two crystals (left); TEM images of the $\alpha(001)$ //Si(001) rectangular and triangular α -FeSi₂ nanoplates

Acknowledgement

The study was carried out with the financial support of the Government of the Russian Federation within the framework of a grant for the creation of world-class laboratories (Agreement No. 075-15-2019-1886).

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MAX Phases as Precursors to New MXenes

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MXenes are potentially the largest class of 2D materials discovered so far. With a general formula of $M_{n+1}X_nT_x$, M is an early transition metal (Ti, V, Nb, Ta, etc.), X is C and/or N, T_x represents the surface groups (-O, -OH, -F, -Cl), and $n = 1-4$, over 30 stoichiometric phases have already been discovered, with many more predicted computationally. This class of materials has been widely studied owing to their exceptional properties, including hydrophilicity, scalability, mechanical strength, thermal stability, redox capability, and ease of processing. Since their discovery, MXenes have been used in a variety of applications, including electrochemical energy storage, electromagnetic interference shielding, biomedical, environmental remediation, catalysis, etc., with more novel applications being studied daily.

Because MXenes inherit their structure from $M_{n+1}AX_n$ (MAX) phase precursors, understanding MAX phase synthesis leads to control over flake size, defect density, and chemical composition of the resultant MXene. One understudied, yet important class of MXenes are solid-solution MXenes, where multiple elements are randomly distributed within the M layers. Solid-solution MXenes exhibit tunable properties that are directly related to their chemistry. By understanding this relationship, it then becomes possible to rationally design new MXenes with specific optical, electronic, and chemical properties. Likewise, solid-solutions can stabilize structures that wouldn't form with only one M element, leading to thicker MXenes ($M_5X_4T_x$) with enhanced thermal stability and optical properties unlike any other MXene.

MAX Phase Nanolaminates: Structure, Transport and Magnetism

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MAX phases are a family of hexagonal, layered compounds with the chemical formula $M_{n+1}AX_n$ ($n = 1-3$) composed of early transition metals M (Sc, Ti, V, Cr, Mn), Main group elements (Al, Ga, Ge, ...) and X (C or N) [1]. Due to their unique structure these materials share properties of ceramics such as high structural stiffness and metals such as good electrical and thermal conductivities [1]. Significant interest in these systems is rising due to a recently discovered possibility of delamination of layered MAX phase structures leading to 2D graphene-like transition metal carbides and nitrides $M_{n+1}X_n$, known as MXenes [2].

We measured the electrical conductivity of 13 nm thick Ti_3C_2 MXene thin films on glass substrate as function of H and O plasma treatment and as function of humidity [3]. It turns out that the resistivities can be switched reproducibly by plasma treatment between $5.6 \mu\Omega m$ (oxidized state) to $4.6 \mu\Omega m$ (reduced state). Both states show metallic conductivity. Moreover, we found a 26-fold increase of the resistivity at relative humidity of 80% as compared to high vacuum conditions [3] leading to possible sensing applications.

In 2013, the new class of magnetic MAX phases was discovered which contain Cr and Mn or a mixture of them as the M element. $(Cr_{0.5}Mn_{0.5})_2GaC$ epitaxial films show a magnetic ordering temperature above 200 K, a very small magneto-crystalline anisotropy energy and a spectroscopic splitting factor of $g = 2.00 \pm 0.02$ [4]. Remarkably, the magnetism of such films is independent of the film thickness and stable in ambient conditions over years [5].

On the way to MAX phases with higher atomic magnetic moments and high ordering temperatures, Mn_2GaC MAX phase epitaxial films have been predicted and successfully synthesized [6]. We studied the magnetic properties of Mn_2GaC films in detail and found two magnetic phase transitions. The Néel temperature is $T_N \approx 507$ K. At $T_t = 214$ K the material undergoes a first order phase transition from AFM above T_t to a non-collinear AFM spin structure. Both states show large uniaxial c -axis magnetostriction of 450 ppm. Of interest, the magnetostriction changes sign, being compressive (negative) above T_t and tensile (positive) below. This sign change across the phase transition is a fundamentally new property, which is a consequence of the layered structure and competing AFM and FM correlations between magnetic atomic layers. This also manifests in the sign switch of the magnetoresistance indicating a coupling between the spin, lattice and electrical transport properties [7].

Acknowledgement

The presented works have been achieved in close collaboration of the University of Duisburg-Essen, Linköping University, and Drexel University. Contributions by R. Salikhov, Iu. P. Novoselova, M. Farle, A. Petruhins, Q. Tao, A. S. Ingason, J. Rosén, and M. Barsoum are gratefully acknowledged. Funding by the Deutsche Forschungsgemeinschaft (DFG) in projects SA3095/2-1 and CRC/TRR 270, B02 (Project-ID 405553726) and the DAAD in the scholarship 57214224 is gratefully acknowledged.

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High-throughput design of magnetic MAX and MAB phases

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Based on high-throughput (HTP) density functional theory calculations, we have investigated systematically the stability of both 2D [1] and 3D [2, 3] MAX (M=Cr, Mn, Fe, Co, Ni; A being a main group element; X=C, N) and MAB [4] phases with nano-laminated crystal structures. In this talk, focusing on the bulk magnetic properties, we demonstrate a generic funnel approach to perform HTP screening, based on the progressive evaluation of thermodynamic, mechanical, dynamical stabilities and on-top characterization of various magnetic properties. After validating the known phases, our HTP calculations predict 20 (21) unreported magnetic MAX (MAB) compounds. Analysis based on the Hume-Rothery rules (Fig. 1) revealed that the valence electron concentration and size factor difference are of significant importance in determining the stability, with good correspondence with the local atomic bonding. Interestingly, we found that MAB phases have more attractive magnetic properties, such as strong magneto-crystalline anisotropy and magnetocaloric performance.

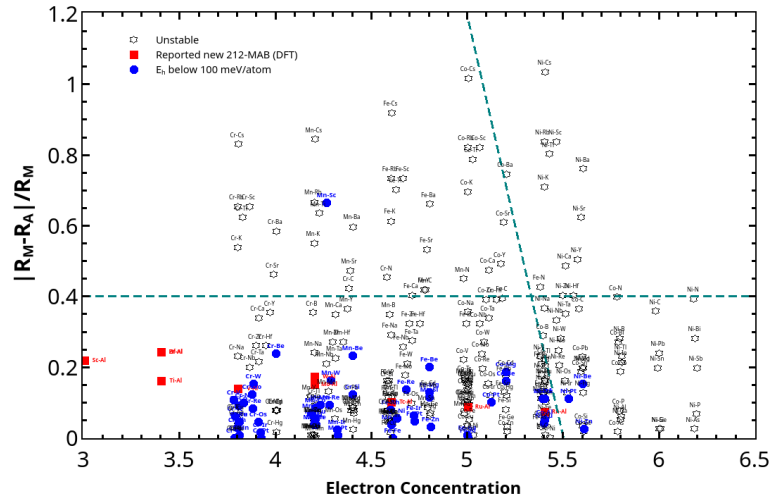


Figure 1: The Hume-Rothery plot marking the stability trend for the 212-MAB compounds.

Acknowledgement

The authors acknowledge support from the LOEWE project RESPONSE funded by the Ministry of Higher Education, Research and the Arts (HMWK) of the Hessen state, and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 405553726 - TRR 270. The Lichtenberg high performance supercomputer of TU Darmstadt is gratefully acknowledged for the computational resources.

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Contributed Presentations (12 + 3 minutes) (alphabetical order)

Effect of the forming gas ALD chamber preconditioning on the physical properties of $\text{TiN}_{1-x}\text{O}_x$ films

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Recently a considerable effort has been dedicated to development of advanced integration technologies of RF components with passive circuits integrated on board by the thin film processing technologies [1]. $\text{TiN}_{1-x}\text{O}_x$ film is a potential candidate for resistors fabrication in such technologies. The self-limiting nature of the ALD growth provides unsurpassed accuracy of the film thickness and uniformity making it promising route to develop the $\text{TiN}_{1-x}\text{O}_x$ resistors for industrial applications. We explored the possibility of the oxygen concentration reduction and process stabilization using the forming gas (FG) pre-treatment of the ALD chamber. We studied the $\text{TiN}_{1-x}\text{O}_x$ films grown with and without FG and compared their physical properties, fabricated $\text{TiN}_{1-x}\text{O}_x$ thin film resistors and explored the temperature dependence of their DC resistance, nonlinearity and aging effect along with their high frequency S-parameters.

$\text{TiN}_{1-x}\text{O}_x$ films were grown at 420°C on glass and (100) silicon wafers by thermal ALD in the Picosun SUNALETM R-200 ADVANCED reactor without load lock. Two groups of samples were grown: G1 – without FG, G2 – with FG. The grown films appeared grey metallic and were used to fabricate RF resistors by combination of the optical lithography, etching and e-beam Ti(5nm)/Cu(1µm) evaporation followed by the lift off for the RF contact pads and ground lines.

The thickness of $\text{TiN}_{1-x}\text{O}_x$ extracted from TEM was equal to 22nm for G1 and 47nm for the G2 samples and their bulk resistivity was 484 µOhm*cm and 202 µOhm*cm. The XPS analysis revealed only 2% difference in the oxygen content of G1 and G2 samples. From the AFM data the grains of G1 were considerably wider (133-196 nm) than those of the G2 sample (9.78 - 10.9 nm). The G2 samples were significantly smoother, (50% smaller RMS). The XRD analysis of the crystal structure revealed that G2 samples had the cell volumes 74.23-74.47 Å³, which was larger than those for the G1 samples (73.86-73.99 Å³). The ellipsometric data of the films optical properties showed increased absorption constant of the samples G2, which is consistent with the higher free carrier concentration in FG pretreated $\text{TiN}_{1-x}\text{O}_x$ films obtained from the Hall measurements: 3,5e22 and 2,2e22 cm⁻³ for the samples with and without forming gas. The s-parameters measurements of G1 resistors showed low resistors mismatch across the wafer (0.1% at the lowest and 10% at the highest frequencies).

Overall the forming gas pretreatment of the ALD chamber prior to the $\text{TiN}_{1-x}\text{O}_x$ film growth significantly reduced the surface roughness and resistivity of the $\text{TiN}_{1-x}\text{O}_x$ film. Based on our experimental data we conclude that this reduction came from combined effect of 2% oxygen content reduction in $\text{TiN}_{1-x}\text{O}_x$ due to redox reaction by FG that caused 50% increase in the free carriers concentration and the surface scattering decrease (possibly due to substantially reduced granularity), which almost doubled the carriers mobility.

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Methods of forming sub- and nanoscale patterns on magnetic thin films

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CMOS and SOI are currently being actively investigated by scientific groups, as a result of which such structures can be easily implemented that can be implemented in electronic devices. The main trend in the development of modern microelectronics is the manufacture of products with submicron-sized elements. Microelectronic technologies are very useful for research applications. In this work, we present an overview of the methods of micro- and nanoscale surface modifications that we use to obtain structures for the study of various physical phenomena and which we successfully use for these purposes.

Many serious studies of a fundamental nature require the formation of a special experimental geometry [1]. Many structures and devices are formed using top-down technology using lithography and chemical etching. Photolithography processes can be used to form devices from continuous films [2] or to create masks through which the material is deposited onto a substrate [3]. The wet chemical etching process is widespread in many areas of science and technology.

Wet chemical etching is used to obtain MXenes from MAX phases [4]. MXenes are 2D family of materials are transition metal carbides, carbonitrides and nitrides [5]. They were named MXenes because the overwhelming majority of them were obtained by etching Al layers from MAX phases. They have exciting physical and chemical properties, have extensive application potential and can be easily obtained in large quantities in water. There are two methods to synthesize 2D materials. The first is a bottom-up approach, such as chemical vapor deposition (CVD) that can produce high-quality films on various substrates. The second approach is a top-down approach, involving the exfoliation of layered solids. MXenes are mostly derived from the MAX phases, in which the M-A layers are quite strongly bound to each other by a combination of covalent and metallic bonds [6]. Therefore, the main problems is finding an appropriate etching solution and selecting a combination of intercalant and solvent.

Acknowledgement

The study was carried out with the financial support of the Government of the Russian Federation within the framework of a grant for the creation of world-class laboratories (Agreement No. 075-15-2019-1886).

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Role of intermediate intermetallics in the formation of MAX phases

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An investigation into the formation of the 312 MAX phase Zr_3AlC_2 , has been performed to develop the understanding of the mechanism of formation in order to create phase pure material. Principally, the investigation focused in the region of 600-900 °C and 1000-1200 °C, to interrogate the formation of the intermediate Zr-Al intermetallics. The effect of the type and concentration of these intermediates on the phase purity of the MAX phase will be discussed and its relation to the heating cycle. The controlled formation of these intermediates has allowed for consistent MAX phase formation, without the inclusion of additional elements such as Si.

We hope that a full understanding of the mechanism of formation of Zr_3AlC_2 will allow the improvement in phase purity of a range of other MAX phases.

How to obtain the dielectric tensor from spectral magneto-optical ellipsometry measurements data

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We have been working on the development of the magneto-optical ellipsometry (ME) technique for its application in the set-up [1], which was designed at Kirensky Institute of Physics for synthesizing thin films with ferromagnetic (FM) layers and analyzing their properties. As a result, we developed the way for finding the dielectric tensor from *in situ* experimental ME data for various models of reflecting FM nanostructures: a model of a homogeneous semi-infinite medium for bulk FM samples on non-magnetic substrates [2]; a model of a FM film on a non-magnetic substrate [3]; a model of a multilayered sample with one FM layer [4].

The approach to data processing was designed especially for the device [1], that is why it is suitable for the analysis of spectral measurements in the optical range in case of the transversal magneto-optical Kerr effect. We took into account that all ellipsometric measurements, including ME measurements, are carried out during one experiment in the same ultrahigh vacuum chamber. We also took into account already well-known methods for the analysis of the diagonal components of the dielectric tensor, for example [5]. Our goal was mainly to relate the data obtained from the set-up (ellipsometric angles and their changes in case of applying magnetic field) and the reflection coefficients for various models, since it is this relationship that determines the off-diagonal components of the dielectric tensor.

Now this technique makes it possible to carry out experimental ME studies on various samples. In the talk we will report on the study of thin polycrystalline Fe/SiO₂/Si films with different thicknesses of the iron layer, including the following points:

1. Materials and data acquisition [6];
2. Processing of ME data using various models of reflecting FM nanostructures
 - Analysis of the role of Fe thickness and penetration depth,
 - Analysis of the influence of SiO₂/Fe and Fe/vacuum interfaces.

As a result of processing the data of spectral ME measurements, the complex diagonal and off-diagonal components of the dielectric tensor of the magnetic layer for Fe/SiO₂/Si samples with different thicknesses of the FM layer in the spectral range of 1.38-3.45 eV were determined. The results obtained are compared with the literature data of other authors and the DFT calculation of the dielectric tensor of Fe.

Acknowledgement

This study was supported by the Research Grant No. 075-15-2019-1886 from the Government of the Russian Federation.

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Prediction of formation of competing phases during the growth of $(\text{Mn}_{1-x}\text{Cr}_x)_2\text{GaC}$ thin films on $\text{MgO}(111)$ with the use of effective heat of formation model and near coincidence site lattice approaches.

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Obtaining the desired properties of the MAX-phases depends on the technological conditions of material synthesis. This requires thorough theoretical modelling of the elements' interaction at the interface. Concurrent growth of competing phases along with a MAX-phase may occur due to the favorability of the formation of competing phases and also be promoted by lower energy interfaces with the substrate in comparison with a MAX-phase. In this work, we study thermodynamic favorability of competing phases and Cr_2GaC and Mn_2GaC MAX-phases depending on the chemical composition of the atomic flow [1]. To study these compounds, it is necessary to consider the Cr-Ga-C and Mn-Ga-C system. The task is to sort through all possible reactions between pure elements, available in quantities correspondent to the given stoichiometry of the MAX-phase, i.e. $\text{Cr}:\text{Ga}:\text{C}=2:1:1$, which is connected with the technological implementation of the synthesis. Moreover, the density of near-coincidence sites [2] for interfaces between MAX-phases, thermodynamically favourable competing phases and $\text{MgO}(111)$ surface is considered to show a role of the interface in the determination of the structural quality of the MAX-phase thin film grown on $\text{MgO}(111)$.

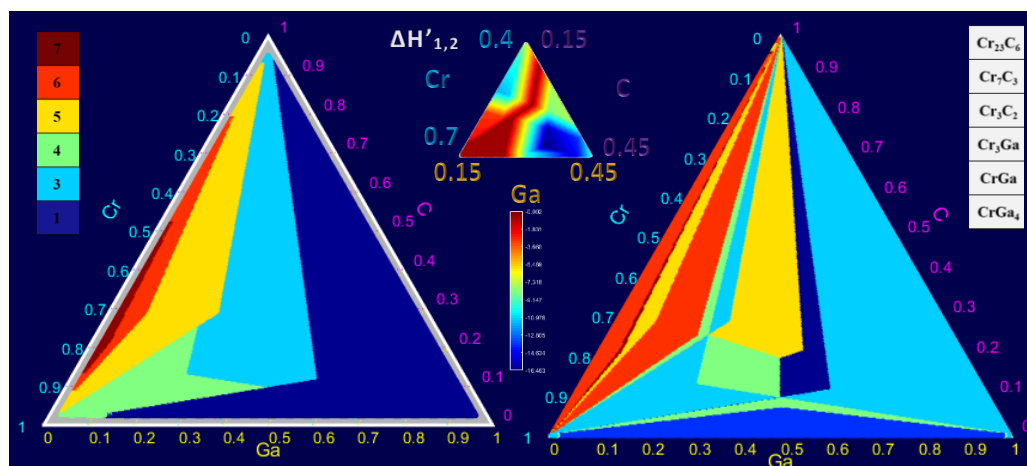


Figure 1. Diagram of the numbers of the most profitable competing phases (in the case of the formation of the MAX phase and one competing phase); (left) the first candidate; (right) the second candidate; in the middle of the figure the difference between the effective heat of formation ($\text{kJ/mol}\cdot\text{atom}$) in case of the most thermodynamically favourable competing phase and the next closest one is depicted.

Acknowledgement

The study was carried out with the financial support of the Government of the Russian Federation within the framework of a grant for the creation of world-class laboratories (Agreement No. 075-15-2019-1886).

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Synthesis and characterization of $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$ MAX-phases with improved manganese doping

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MAX-phases – the novel class of nano-laminated ternary borides, carbides and nitrides – have recently gained interest due to their unique combination of metallic and ceramic properties [1]. Plenty of work has been done on the search and synthesis of magnetic MAX-phases that can be applied in the variety of practical fields, including spintronics. One of the possible candidates is $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$; in this phase a competition of ferro- and antiferromagnetic interactions, possibly leading to non-collinear types of the magnetic ordering, was demonstrated [2]. However, manganese atoms are poorly incorporated to the MAX-phase structure, thus the maximum doping level, achieved so far for bulk samples, equaled 10 at.% when the non-trivial method of microwave heating was exploited [3]. As manganese addition induces an obvious worsening of the samples' quality [4], it is therefore challenging to produce $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$ MAX-phase in pure-phase bulk form.

Here we present a study on the possibility to produce highly pure $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$, in bulk form and with the highest level of manganese doping. The arc melting technique [5] was used as the effect of the high-energetic plasma was proved helpful for the production of the same compounds in thin film form [6]. The synthesis protocol was completely optimized to increase the total MAX-phase outcome in the resulting bulk samples, while minimizing the amount of by-phases appearing at this stage. Intermetallic side phases that could not be eliminated via the tuning of the synthesis conditions were next dissolved in the HF acid solution. The use of the optimized protocol and the ability to successfully get rid of side phases made possible to produce $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$ MAX-phase solid solutions with doping levels reaching about 20 at.%. All the samples were checked for morphology by scanning electron microscopy and analyzed using powder X-ray diffraction and energy-dispersive spectroscopy analysis. The effect of the manganese addition on the structural properties was also studied.

Acknowledgement

We acknowledge the Russian Foundation of Fundamental Research for the provided financial support through the grant № 19-32-50138.

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Epitaxial growth of Cr₂AlC MAX phase thin films by pulsed laser deposition

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MAX phases (M_{n+1}AX_n) are ternary or quaternary compounds of layered hexagonal structures, where M is an early transition metal, A is an A group element and X is either C or N [1]. Within the last years, much attention has been put on magnetic MAX phases with Cr and/or Mn as two possible M elements. The magnetic properties of such (M_{1-x}M₂)₂AX phases are driven by competing ferromagnetic and antiferromagnetic correlations leading to complicated phase diagrams [2,3]. One parent compound of such MAX phases is Cr₂AlC.

In this work, we show the first successful synthesis of epitaxial Cr₂AlC thin films on MgO(111) and Al₂O₃(0001) substrates by pulsed laser deposition (PLD) at 600°C with film thicknesses of 10-50 nm. The used KrF Laser (248 nm) hits the 3 elemental targets at an energy density of 13 J cm⁻². Figure 1 presents X-ray diffractograms of 20 nm epitaxial films, simultaneously grown on MgO(111) and Al₂O₃(0001), and the corresponding pole figure of the epitaxial Cr₂AlC films on MgO(111). Cr₂AlC can be easily doped by additional magnetic elements from the 3d series.

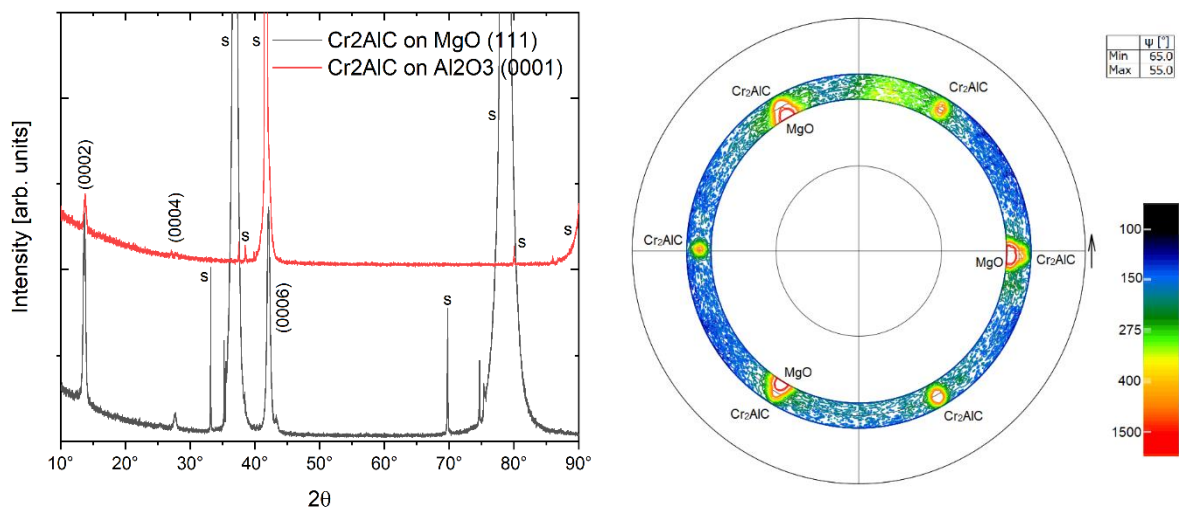


Figure 1. X-ray diffractograms of 20 nm epitaxial Cr₂AlC films on MgO(111) and Al₂O₃(0001), and the corresponding pole figure on the Cr₂AlC [10 $\bar{1}$ 3] Bragg peaks of the 20 nm film on MgO(111).

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Modification of optical and magneto-optical response of highly textured $\text{Au}_3\text{Fe}_{1-x}/\text{Fe}$ Janus-like nanocrystals grown on amorphous silicon dioxide surface

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A distinctive feature of Au insolubility in Fe allows the formation of thin Au shells on the surface of Fe nanocrystals due to phase segregation at high temperatures. That the ordered and disordered phases of intermetallic Au-Fe compounds with different magnetic characteristics depending on the composition can exist in Au-Fe nanoscale systems.

We present a route to produce highly-textured $\text{Au}_3\text{Fe}_{1-x}(111)/\text{Fe}(110)$ hybrid and pure $\text{Au}_3\text{Fe}_{1-x}(111)$ nanocrystals on an amorphous surface of SiO_2/Si by molecular beam epitaxy. It is possible to tune the average lateral and vertical size of the resultant nanocrystals from 10-20 nm up to 100-150 nm at the same Fe nominal thickness deposited by controlling the quantity of Au atoms preliminary deposited onto the SiO_2/Si surface. This process is sensitive to the initial density and size of Au islands. Modification of optical and magneto-optical response due to the changes in the morphology and phase composition of the nanocrystal ensembles is under investigation with the use of experimental and simulation techniques.

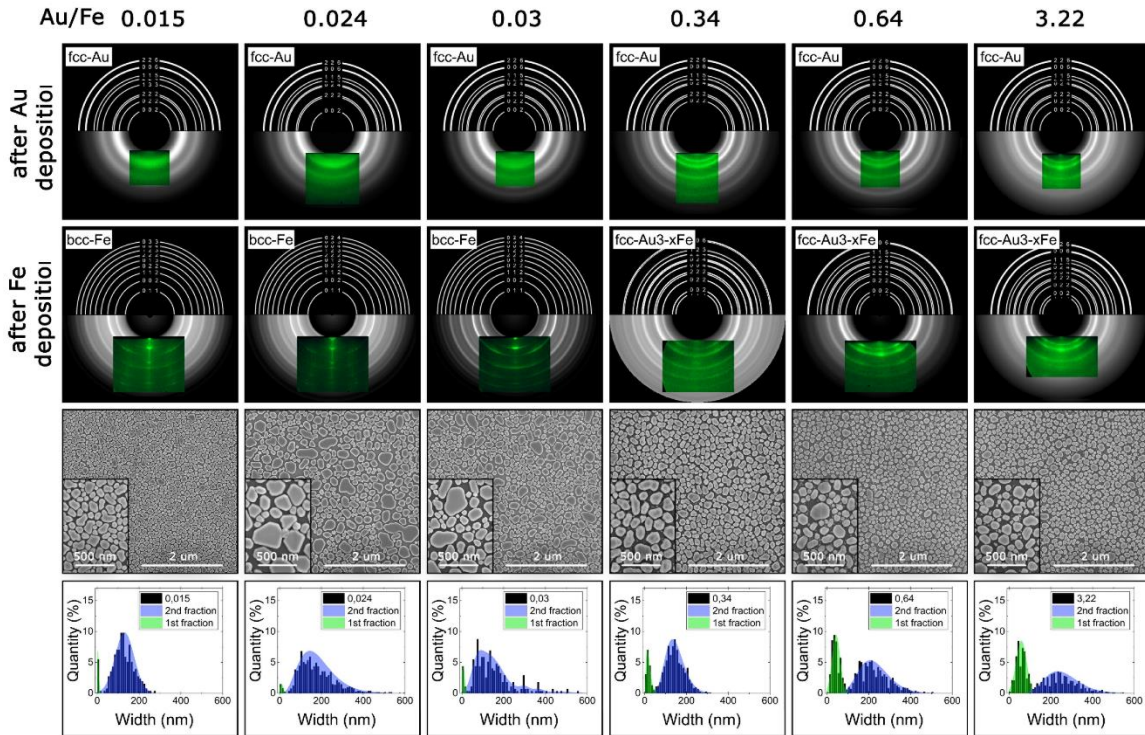


Figure 1. RHEED patterns, SEM images and statistical analysis of the lateral size of $\text{Au}_3\text{Fe}_{1-x}(111)/\text{Fe}(110)$ hybrid nanocrystals obtained with different predeposited Au layer.

Acknowledgement

The study was carried out with the financial support of the Government of the Russian Federation within the framework of a grant for the creation of world-class laboratories (Agreement No. 075-15-2019-1886).