Our theoretical group performs the research devoted to the study of different aspects of application of quantum mechanical and statistical thermodynamics approaches to the analysis of the properties of solid bulk materials, surfaces and the interfaces. The research is based mainly on the Density Functional Theory (DFT) which is considered nowadays as one of the most powerful tools in the study of the nature of bonding in materials.

The topics that are intensively investigated in the group are:
a) Structure and properties of the interfaces; b) Stability of intermetallic compounds; c)Thermodynamics and kinetics of phase transitions in metallic alloys and perovskites; d) theoretical aspects of wetting phenomena; e) adsorption in catalysis; f) growth of thin metallic films.

The work is carried out in collaboration with Profs. N. Frage, M. Landau, A. Kiv, E. Glikman, N. Froumin, Dr. Sh. Barzilai. Several MSc and PhD students are also involved in this activity. Following are several examples of the performed researches.

1. The main idea that consolidates different subjects of investigations b), c), d) and f) is based on considering the atomic system of interest in the effective field of surrounding atoms. For the analysis of thin film growth it is a metal atomic layer in the field of the substrate, for perovskite solid solutions it is the sub-lattice of A atoms, where A-Metal substitutional solid solution is formed, in the field of the rest B and O atoms. A nice example of application of this approach is the explanation of the morphology of extra-thin Ag or Cu films on MgO substrate – the spinodal decomposition of the 2D metal atom-"empty site" solid solution in the field of the substrate allows estimating the concentration and temperature regions when the metal islands are formed on the surface of MgO. Further Monte Carlo simulations support this finding. Application of the statistical thermodynamics methods enable considering the shape of the growing metal nano-rods on the ceramic surface.

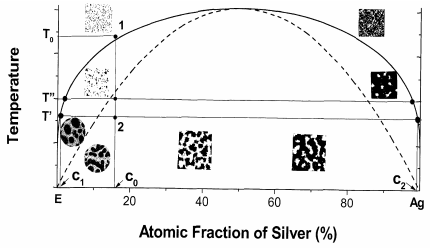



Fig. 1. Modes of the Ag film growth on MgO at moderate temperatures on phase diagram. Binodal and spinodal curves are shown as solid and dashed lines, respectively. Black areas in inserts are Ag, grey MgO.

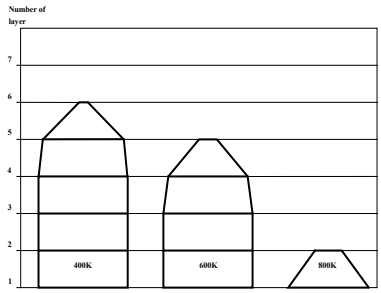



Fig. 2. Schematic shape of 3D Cu cluster formed on MgO at three different temperatures.

Another example is the study of $TiC_cN_{1-c}$ solid solutions. Complete set of totally ordered structures in $TiC_cN_{1-c}$ that are stable with respect to formation of anti-phase domains was considered. The calculations of the formation energies were carried out in the framework of the linearized augmented plane wave (LAPW) method as implemented in Wien2k code. The energetically preferable phases were determined for the stoichiometric compositions, $c_{st}$=1/8, 7/8, 1/4, 3/4, and 1/2. Using the Concentration Wave approach the Fourier transforms of the mixing potential were extracted for these phases from ab initio calculations. The obtained data is applied to analyze temperature dependencies of long range order parameters for the phases where the ordering is described by one or two order parameters. Low temperatures for

the order–disorder phase transformations are obtained. This explains the difficulties in experimental study of the low-temperature phase diagram due to frozen kinetics: the time scales on which equilibration to the thermodynamically stable phase takes place exceed the time available for the experiment.

Latest publications:


1.Yu. F. Zhukovskii, E. Kotomin, D. Fuks, S. Dorfman, A. M. Stoneham, G. Borstel, Adhesion trends and growth mode of ultra-thin copper films on MgO, J. of Phys.: Condens. Matter, **16,** pp. 4881-4896, 2004.

2.D. Fuks, S. Dorfman, S. Piskunov, E. Kotomin, *Ab initio* thermodynamics of $Ba_cSr_{(1-c)}TiO_3$ solid solutions, Phys. Rev. B, **71**, 014111-1-9, 2005.

3.D. Fuks, Yu. F. Zhukovskii, E. A. Kotomin, D. E. Ellis, Metal film growth on regular and defective MgO(001) surface: A comparative *ab initio* simulation and thermodynamic study, Surf. Sci., **600**, pp. L99-L104, 2006.

4.D. Vingurt, D. Fuks, *Ab initio* study of low-temperature phase transformations in ternary solid solution $TiC_cN_{1-c}$, Intermetallics, **18**, pp. 359-368, 2010.


2. A remarkable decrease of the contact angle between the metal melt and $CaF_2$ solid substrate occurs when small amounts of Ti are added to liquid In, while a relatively small change of the contact angle is observed when it was added to liquid Sn. In order to understand the reason for this different behavior, *ab-initio* calculations were carried out in the framework of DFT. The results of the calculations indicate that the level of the interaction between the Me and the Ti atom affects the (Me-Ti)/$CaF_2$ interface composition, the interfacial energy and the wetting behavior. For the system with stronger interatomic attraction in the melt (Sn-Ti alloys), Ti atoms prefer to be surrounded by Sn atoms, and only weakly affect the metal/substrate interfacial energy and, thus the observed contact angle. However, for weak interatomic attraction (In-Ti alloys) an enhanced Ti adsorption at the metal/substrate interface takes place and leads to decrease the interfacial energy and improved wetting. The differences in the wetting behavior for these systems are analyzed in terms of the total energy of each system, the electron charge re-distribution and the electron Density of States (DOS).

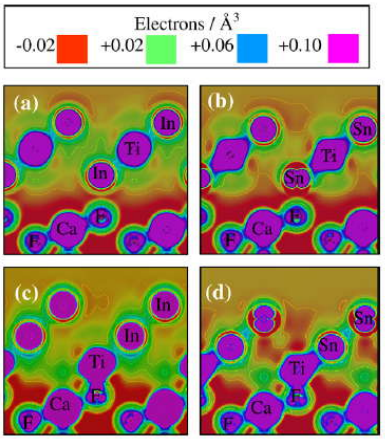
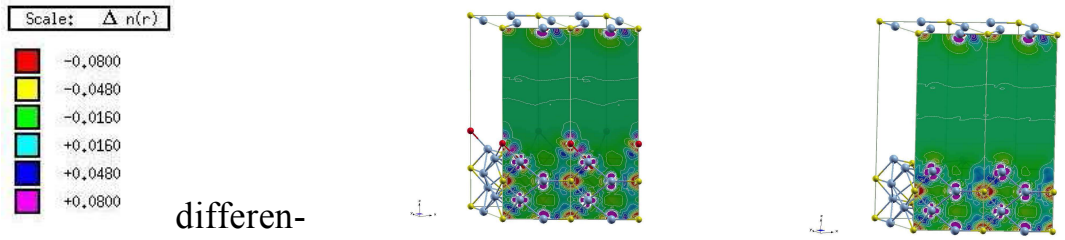



Fig. 3. The differential electron densities (the differences between the electron density of the system and the sum of the electron densities of the individual atoms) illustrating the formation of bonding. Three layers of metal atoms in two kinds of atomic arrangements atop $CaF_2$ (111)-terminated slab are shown: (a,b) 1monolayer (ML) of Ti between two layers of In or Sn atoms, and (c,d) 1 ML of Ti at the interface between two layers of In or Sn and the slab.

Latest publications:

1. S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, First-principles modeling of metal layer adsorption on $CaF_2$ (111), Surf. Sci., **602**, pp. 1517-1524, 2008.
2. S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, The effect of the Ti on the wetting of $CaF_2$ substrate by In-Ti and Ga-Ti alloys. Ab-initio consideration, Appl. Phys., A: Materials Science and Processing, **93**, pp. 379-385, 2008.
3. S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, The effect of Me-Ti inter-atomic interactions on wetting in $CaF_2$/(Me-Ti) systems: *ab-initio* considerations, Surf. Sci., **603**, pp. 2096–2101, 2009.

3. DFT was applied to calculate the adsorption energies for S adatoms adsorbed on the surface of $Ni_2P$, $Ni_{12}P_5$ and $Ni_3P$ phases. The preferable (001) surface-terminated slabs were determined to link the coverage tendency with the peculiarities of the DOS at the Fermi energy. The electron charge re-distribution due to the adsorption of S atoms is calculated and the nature of bonding of S with the substrates is discussed. The combination of *ab-initio* calculations performed in the ground state for the considered systems with statistical thermodynamics renders the possibility to obtain the coverage at the temperatures beyond T = 0 K in good agreement with experimental data. The increasing of surface coverage of $Ni_xP$ phases with increasing the x value is the result of fine interplay between the number of possible sites for S adsorption and the difference in the adsorption energies for these sites.




differential density

a) b)

Fig. 4. Differential electron density (in e/Å$^3$) maps illustrating the formation of bonds between the adsorbed sulfur atom and $Ni_2P$ (001) substrate surface: a) the charge distribution in the presence of adsorbed S atom; b) the same without S atom.

Latest publications:

1. M. Landau, M. Herskowitz, T. Hoffman, D. Fuks, E. Liverts, D. Vingurt, N. Froumin, Ultradeep hydrodesulfurization and adsorptive desulfurization of diesel fuel on metal-rich nickel phosphides, Industrial & Engineering Chemistry Research, **48** (11), pp 5239–5249, 2009
2. D. Fuks, D. Vingurt, M. Landau, M. Herskowitz, DFT study of sulfur adsorption at the (001) surface of metal-rich nickel phosphides: effect of Ni/P ratio, J. Phys. Chem. C, **114 (31)**, pp.13313–13321, 2010.