

## Highlights of research 2008

Our research involves first principles quantum mechanical investigations into the properties of materials and their surfaces for systems of high relevance to technological applications, as well as of fundamental interest; for example:

1. Heterogeneous catalysts for energy production, manufacturing, and emission control
2. Engineering nitride-based dilute magnetic semiconductor interfaces for potential spintronics applications
3. Fundamental investigations into the physics of gas-surface interactions and adsorption

Below are some highlights of work done over the last year:

### ***Understanding Iridium-based catalysts on the atomic scale***

Obtaining a detailed knowledge of the surface structure and stoichiometry is crucial for understanding the physical and chemical properties of advanced materials such as those used in heterogeneous catalysis, corrosion resistance, electronic devices, sensors, and fuel cells. This knowledge is also central for enhancing the performance of existing catalysts as well as developing new ones. Many current industrial processes involve catalytic oxidation reactions, where the catalysts are typically transition metal particles dispersed on oxide supports. The importance of transition metals (TMs) for such reactions has motivated large numbers of studies on oxygen-metal interactions at low index surfaces of TMs with the aim of obtaining a better understanding of the underlying mechanisms on the atomic scale.

As a late *5d* transition metal, iridium shows potential in a great variety of applications, particularly as a heterogeneous catalyst in various industrial chemical reactions. With the increased demand for clean alternative energy, iridium is seen as a potential catalyst for CO<sub>x</sub>-free production of hydrogen from ammonia and gasoline to be used as fuel in automobile fuel cells. In addition, it is also considered as an improvement to the automobile catalytic converter because of its unique ability to decompose NO as well as reduce NO<sub>x</sub> in the presence of hydrocarbons. Clearly, an atomic-level understanding of the interactions of these gas phase species with Ir surfaces would be very valuable, and could lead to improved Ir-based catalysts. We have initially focussed on the interaction of oxygen with the (111) surface of Ir, and through first-principles calculations we determined the pressure-temperature phase diagram (see Figure 1) for conditions extending from ultrahigh vacuum to those typical of technical catalysis.

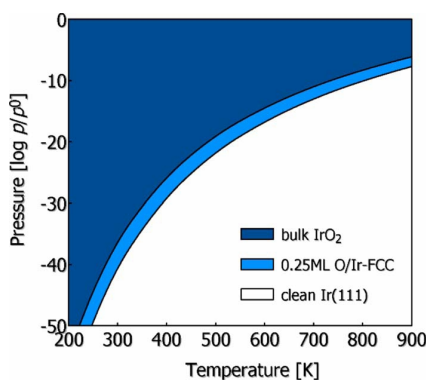


Figure 1: Surface ( $p, T$ ) phase diagram showing the stability range of the lowest energy structures.

Such phase-diagrams predict the stable surface atomic structure and composition for a given oxygen partial pressure and system temperature. Our results show that there are only three thermodynamically stable regions, namely, the clean Ir(111) surface, the ordered (2x2) oxygen adsorption phase, and bulk iridium oxide. Interestingly, our study reveals that a thin trilayer (O-Ir-O) surface oxide-like structure (see Figure 2) is rather low in energy and is

metastable in the region that the bulk oxide is predicted. This suggests that should the formation of the bulk oxide be kinetically hindered (e.g. due to the presence of energy activation barriers) then, this phases could be present on the Ir catalyst surface under technical conditions close to those of the real catalysts. This prediction, was in fact recently

verified by experimental work.

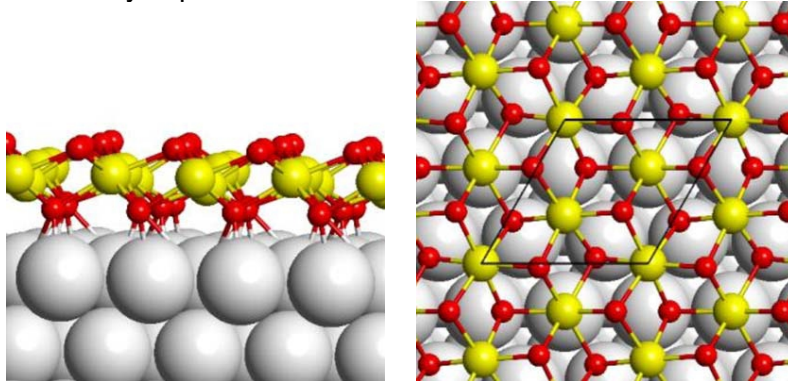


Figure 2: The reconstructed surface-oxide-like trilayer structure. Oxygen atoms are shown as small dark (red) spheres, while the small gray (yellow) spheres are the uppermost Iridium atoms in the trilayer. The large gray spheres are the second and third layer (unreconstructed) iridium atoms. The surface unit cell is indicated.

### ***Built-in electric field assisted spin injection in Cr and Mn $\delta$ -layer doped AlN/GaN(0001) heterostructures from first-principles***

Recently, there has been a rapidly growing interest in the field of semiconductor spintronics, which aims to add spin-dependent functionality and enhanced performance to the existing principles of electronic device operation. One of the crucial prerequisites, and still a challenge, for successful implementation of this concept is the ability to create a desired spin orientation of carriers and to transport them in a semiconductor to an active region of a device with minimum loss of spin-polarization. Traditionally, spin-polarized electrons have been created in semiconductors simply by illuminating the materials with circularly polarized light so that spin-polarized electrons with a preferred spin direction are excited, following the optical selection rules, enabling the generation of a spin-polarized current. For practical spintronic device applications, however, electrical *spin injection* is required. Electrical spin injection requires a contact material as the spin source, or spin aligner, and a corresponding interface that facilitates the transport of spin-polarized carriers into the semiconductor.

The search for efficient spin injection contact materials falls broadly into two categories. One natural approach is to use ferromagnetic (FM) metal electrodes, such as Fe, which have a high Curie temperature ( $T_c$ ). The other approach is to use diluted magnetic semiconductors (DMSs). Recently we have carried out extensive first-principles density-functional theory calculations to investigate the feasibility of using Cr- and Mn-doped wurtzite polar AlN/GaN(0001) heterostructures for efficient electrical spin injection systems (see Figure 3).

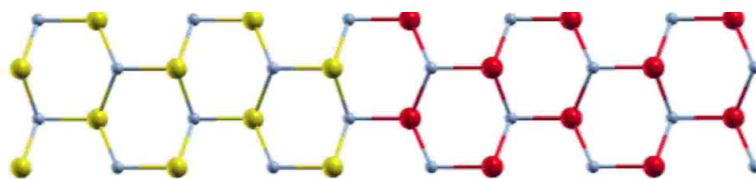


Figure 3: Atomic structure of the studied host semiconductor heterojunction. Small (blue) spheres indicate N atoms and large light (yellow) and dark (red) spheres indicate Al and Ga atoms, respectively. Cr and Mn dopants occupying all the Al and Ga sites are considered.

To overcome the formation of detrimental embedded clusters, we propose digital  $\delta$ -layer doping perpendicular to the growth direction so as to realize enhanced performance at room temperature, and achieve the desired half-metallic character with 100% spin-polarization. We investigated the formation energy, electronic and magnetic properties, and the degree of spin polarization for both neutral and charged valence states for various dopant concentrations. Our results show that under both metal-rich (Al- or Ga-rich) and N-rich conditions, Cr and Mn dopants prefer to segregate into the GaN region and reside close to the interface. Spin injection channels are constructed via the hybridization between dopant  $3d$  and surrounding host atoms, up to a few monolayers around the interface, where the spin-polarized  $t_2$  electrons are injected into the AlN region (see Figure 4).

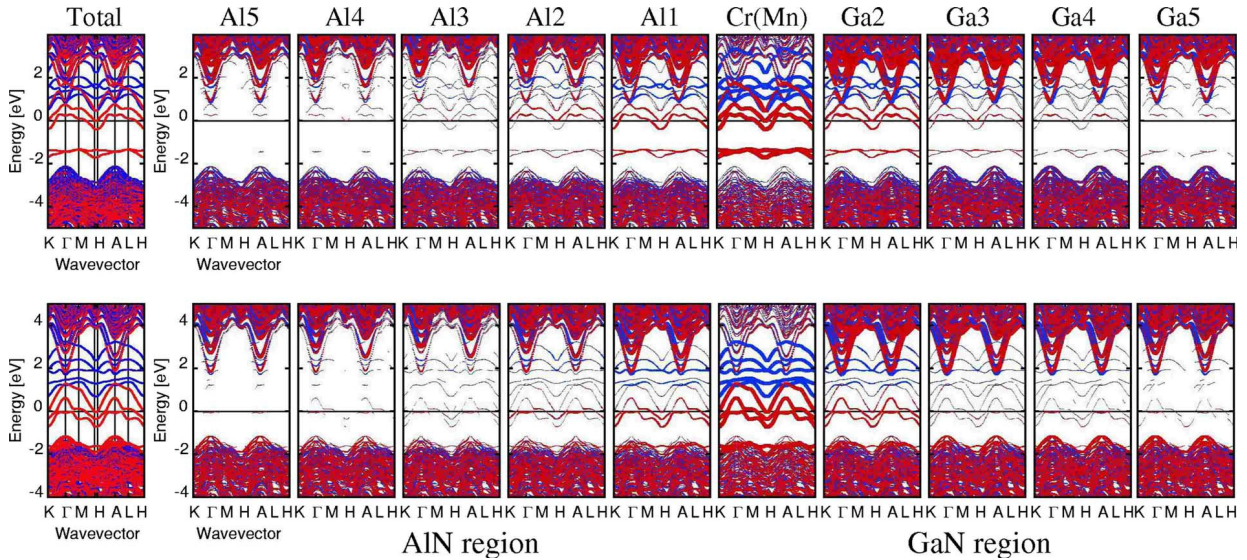


Figure 4: Total and atom-resolved band structures for Cr- (upper panel) and Mn-doped (lower panel) AlN/GaN(0001) heterostructures at the concentration of 1/2 ML. Red denotes majority bands, and blue denotes minority bands.

Significantly, for the energetically favorable configurations, the built-in electric field in the AlN/GaN(0001) heterointerface serves as a driving force for efficient spin injection through the interface and spin transport in the AlN region (see Figure 5). Also importantly, the electronic properties of the heterostructures (half metallic, semiconducting, or metallic) are found to depend sensitively upon the doping concentration and valence charge states.

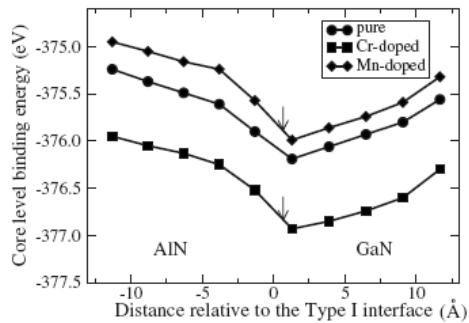


Figure 5: Nitrogen 1s core-level binding energies in pure and Cr and Mn-doped AlN/GaN(0001) heterostructures, demonstrating the presence of the built-in electric field. The arrows indicate the energetically most favorable  $\delta$ -layer doping positions.

### Trends and understanding of rare-gas atom (He, Ne, Ar, Kr, Xe) adsorption on the Pd(111) surface

It was recently found from *ab initio* investigations [J. L. F. Da Silva *et al.*, Phys. Rev. Lett. 90, 066104 (2003)] that polarization effects and the site dependence of the Pauli repulsion largely dictate the nature of the interaction and the site preference of Xe adatoms on close-packed metal surfaces. It is unclear if the same interaction mechanism occurs for *all* rare-gas atoms adsorbed on such surfaces. To address this question, we performed all-electron density functional theory calculations for He, Ne, Ar, Kr, and Xe on Pd(111). Our results confirm that polarization effects of the rare-gas adatoms and Pd atoms in the topmost surface layer (see Figure 6), together with the site-dependent Pauli repulsion, largely determine the interaction between rare-gas atoms and the surface. Similar to our earlier *ab initio* study mentioned above, the on-top site preference is obtained, which was hitherto completely unexpected based on early understanding.

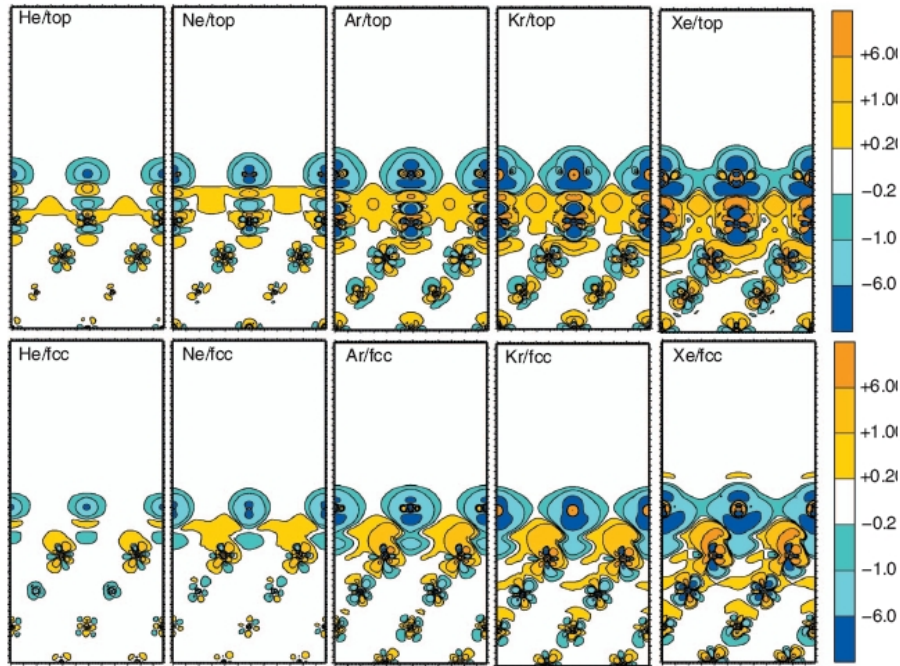


Figure 7: Difference electron density distributions for He, Ne, Ar, Kr, and Xe (from left to right) adatoms on the Pd(111) surface in the on-top (upper) and fcc (lower) sites. Yellow, gold, and orange (cyan, sky blue, and blue) indicate regions where the electron density increases (decreases).

### Publications since the start of 2008

1. J. L. F. Da Silva and C. Stampfl, Trends in rare-gas atom (He, Ne, Ar, Kr, Xe) adsorption on the Pd(111)-( $\sqrt{3} \times \sqrt{3}$ )R30°: An all-electron density-functional theory study, *Phys. Rev. B* 77, 045401 (2008)
2. S. Piccinin, C. Stampfl, and M. Scheffler, First-principles investigation of Ag-Cu alloy surfaces in and oxidizing environment, *Phys. Rev. B* 77, 075426 (2008).
3. A. Das Arulsamy, A. Soon and C. Stampfl, Transport properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> superconductors and electronic structure of Cu<sub>2</sub>O surfaces, to appear in YBCO Superconductors Research Advances, NOVA Science Publishers, New York (2008), accepted.
4. D. J. Carter, J. D. Gale, B. Delley, and C. Stampfl, Geometry and diameter dependence of the electronic and physical properties of Gallium Nitride nanowires from first principles, *Phys. Rev. B* 77, 115349 (2008).
5. A. Soon, L. Wong, B. Delley, and C. Stampfl, Morphology of copper particles in a nitrogen atmosphere: A first-principles investigation, *Phys. Rev. B* 77, 125423 (2008).
6. H. Q. Shi and C. Stampfl, Shape and surface structure of gold nanoparticles under oxidizing conditions, *Phys. Rev. B*, 77, 094127 (2008).
7. H. Zhang, A. Soon, B. Delley, and C. Stampfl, Aluminum adsorption on Ir(111) at a quarter monolayer coverage: A first-principles study, *Appl. Surf. Sci.*, 254, 7655 (2008).
8. X. M. Duan and C. Stampfl, Nitrogen vacancies in InN: Vacancy clustering and metallic bond-like formation from first-principles, *Phys. Rev. B*, 77, 115207 (2008).
9. C. Stampfl, A. Soon, S. Piccinin, H. Q. Shi and H. Zhang, Bridging the temperature and pressure gaps: Close-packed transition metal surfaces in an oxygen environment, *J. Phys.: Conden. Matter*, 20, 184021 (2008).
10. H. Zhang, A. Soon, B. Delley, and C. Stampfl, Stability, structure and electronic properties of chemisorbed oxygen and thin surface oxides on Ir(111), *Phys. Rev. B* 78, 045436 (2008).
11. X. M. Duan and C. Stampfl, Vacancies and interstitials in Indium Nitride: Vacancy clustering and molecular bond-like formation from first-principles, *Phys. Rev. B*, accepted.
12. S. Piccinin, C. Stampfl, and M. Scheffler, Ag-Cu alloy surfaces in an oxidizing environment: a first-principles study, *Surf. Sci.* 603, 1467 (2009).
13. X.-Y. Cui, J. E. Medvedeva, B. Delley, A. J. Freeman, and C. Stampfl, Built-in electric field assisted spin injection in Cr and Mn  $\delta$ -layer doped AlN/GaN(0001) heterostructures from

- first-principles, Phys. Rev. B, 78, 245317 (2008).
14. A. Soon, X.-Y. Cui, Bernard Delley, Su-Huai Wei, and Catherine Stampfl, Native defect-induced multifarious magnetism in nonstoichiometric cuprous oxide: First-principles study of bulk and surface properties of  $\text{Cu}_{2-x}\text{O}$ , Phys. Rev. B 79 035205 (2009)
  15. X. M. Duan and C. Stampfl, Defect complexes and cluster doping of InN: First-principles investigations Phys. Rev. B 79, 035207 (2009)
  16. D. J. Carter and C. Stampfl, Atomic and electronic structure of single and multiple vacancies in GaN nanowires from first-principles, Phys. Rev. B 79, 195302 (2009)
  17. X. M. Duan and C. Stampfl, Co-doping of aluminium and gallium with nitrogen in ZnO: A comparative first-principles investigation, accepted in Phys. Rev. B
  18. X. Y. Cui, B. Delley, A. J. Freeman and C. Stampfl, Tunnel magnetoresistance in trilayer junctions from first-principles: Cr -layer doped GaN/AlN/GaN (0001). submitted to Phys. Rev. B
  19. X. Y. Cui, B. Delley, A. J. Freeman and C. Stampfl, First-principles investigation of Mn -layer doped GaN/AlN/GaN (0001) tunneling junctions submitted to J. Appl. Phys.
  20. C. Stampfl and D. Carter, Book Chapter, Gallium Nitride Nanowires, To appear in the Handbook of Nanophysics. Editor K. Sattler, Taylor & Francis
  21. M. Fronzi, A. Soon, B. Delley, E. Traversa, and C. Stampfl, Stability and morphology of cerium oxide surfaces in an oxidizing environment: A first-principles investigation, submitted to J. Chem. Phys.
  22. M. Fronzi, S. Piccinin, B. Delley, E. Traversa, and C. Stampfl, Water adsorption on the stoichiometric and reduced  $\text{CeO}_2(111)$  surface: A first-principles investigation, submitted to J. Phys. Chem. Chem. Phys.
  23. M. Altarawneh, M. W. Radny, P. V. Smith, J. C. Mackie, E. M. Kennedy, B. Z. Dlugogorski, A. Soon, and C. Stampfl, 2-Chlorophenol Adsorption on  $\text{Cu}_2\text{O}(110)\text{CuO}$ : A First-Principles Density-Functional Study, accepted for publication in J. Chem. Phys.