Annual Report

Our group’s focus is on \textit{ab initio} investigations of materials and surface science phenomena of systems of relevance to technological applications, as well as of fundamental interest. Over the last year, our research activities include:

1. Copper-, gold-, and ceria-based catalysts for energy production, manufacturing, and emission control
2. Nitride-based semiconductor materials for spintronic and optoelectronic devices
3. Superhard nitride-based coatings for mechanical cutting tools as well as fundamental studies of metal surfaces.

Below are some highlights of recent publications:

**Copper-based Catalysis for Energy Production**

In recent years there has been great focus on clean and efficient energy technology, bringing about an increased interest in key heterogeneous catalytic reactions associated with, e.g., the function of fuel cells. An example is the water-gas-shift reaction where hydrogen (fuel) is obtained via partial oxidation and steam reforming of hydrocarbons and methanol. For these reactions, copper-based catalysts are typically employed, but the active site, the role of support oxides, and each detailed reaction step are still the focus of considerable debate. This is so even though a great deal of effort has gone into seeking consensus by conducting \textit{in situ} experiments, in the hope of bridging the “pressure” and “materials” gap. Clearly, in order to achieve more efficient and selective catalysts, knowledge of the microscopic behavior is mandatory.

![Surface free energies of various copper oxide surface terminations as a function of the oxygen chemical potential, as correlated with the pressure for three selected temperatures of interest (from Ref. [9]).](image)

Figure 1: Surface free energies of various copper oxide surface terminations as a function of the oxygen chemical potential, as correlated with the pressure for three selected temperatures of interest (from Ref. [9]).
To gain an initial microscopic understanding of copper-based catalysts, we performed state-of-the-art quantum mechanical calculations, investigating the detailed interaction of oxygen and copper, and focusing on the relative stability of surface oxidic structures and oxide surfaces of the O/Cu system. By combining the concepts of quantum mechanics and thermodynamics in so-called “first–principles atomistic thermodynamics”, we study the chemisorption of oxygen and the formation of sub-nano films of oxidic structures on the (111) surface of copper by including the temperature and pressure dependence of the oxygen chemical potential. These oxidic structures, which resemble the (111) surface of bulk Cu$_2$O, are stable under ultra-high vacuum conditions, but are only metastable at pressures and temperatures relevant to technical catalysis. Further, no simple oxygen chemisorption phase is stable even at very low coverages [2,7]. Under realistic conditions, the bulk oxide phase is predicted to be the most stable phase. Investigating, therefore, the thermodynamic stability of low index (100), (110), and (111) surfaces of bulk Cu$_2$O, including the stoichiometric, as well as metal- and oxygen-rich terminations, and defective surfaces, we find that under the oxygen-rich conditions, two structures exhibit particularly low surface free energies, namely, the Cu$_2$O(110) surface which is terminated with both Cu and O surface atoms in the [110] plane and the Cu$_2$O(111) surface containing a surface Cu vacancy (see Fig. 2). These structures therefore could be catalytically relevant for oxidizing reactions. Studies of these systems are continuing in 2007.

Nitride-based Materials for Spintronic Devices

Dilute magnetic semiconductors (DMS), such as Mn-doped GaAs and Cr-doped GaN, are a class of materials that increasingly attract intense interest as promising candidates for a new generation of multifunctional spintronics devices. Despite considerable efforts, the mechanisms behind the apparent ferromagnetism and the universality are still under active debate. From a fundamental standpoint, DMSs also present a unique type of system which offers the possibility of studying the interaction between the delocalized band electrons of the host semiconductor and the localized d-band electrons of the magnetic transition metal (TM) ions, and consequently the magnetic phenomena, with a relatively simple bandstructure. One characteristic feature associated with TM doped III-V(N) semiconductors is that the host-bandgap serves as the “arena” for the localized TM-d-band electrons, in which the Fermi level is typically located. This, in principle, facilitates the possibility to tune the magnetic behavior by external perturbations.

Through first-principles density-functional theory calculations for isolated transition metal doped GaN (TM=V, Cr, Mn, Fe, Co, Ni on cation sites), we have discovered a novel magnetic metastability in dilute magnetic semiconductors for the first time: Besides the expected ground high spin (HS) states (4 $\mu_B$/Mn and 5 $\mu_B$/Fe), there are also metastable low spin (LS) states (0 $\mu_B$/Mn and 1 $\mu_B$/Fe), see Fig. 3. This phenomenon can be explained in simple terms on the basis of ligand field theory. The transition between the HS and LS states corresponds to an intra-ionic transfer of two electrons between the $t_2$ and $e$ orbitals, accompanied by a spin-flip process. The results suggest that TM-doped wide-band semiconductors (such as GaN and AlN) may present a new type of light-induced spin-crossover materials [5].
Nitride-based Superhard Nanocomposites

There has been considerable effort in recent years in identifying and developing new and improved super- and ultra-hard materials. Such structures clearly have huge potential technological and industrial applications, but are also of fundamental interest with regard to understanding the mechanisms responsible for the enhanced hardness. In particular, the most challenging quest, to find a material harder, more stable, and oxidation resistant than diamond (hardness \( \cong 90 \) GPa), is proving elusive. One strategy, however, that has lead to reported hardnesses equal to, and exceeding, that of diamond is based upon a generic design concept involving self-organized spinodal phase segregation, leading to a nanocomposite, "\( nc-\text{TiN}/ a-\text{Si}_3\text{N}_4/a-\text{and } nc-\text{TiSi}_2\)”, with strong, sharp interfaces between nanocrystalline regions (of TiN and TiSi\(_2\)) and thin amorphous layers (of Si\(_x\)N\(_y\)). The related, more simple quasi-binary nanocomposite, "\( nc-\text{TiN}/ a-\text{Si}_3\text{N}_4\)”, which exhibits a reported superhardness of 50-60 GPa, is the most quantitatively studied and may be regarded as the “prototype” or “model system” for the nitride-based nanocomposites. The hardness of the constituent materials, TiN and Si\(_3\)N\(_4\) is only around 20 GPa, so a notable hardness enhancement occurs for these composites. There are, however, conflicting reports for the hardness of this material, in particular notably lower values of 30-35 GPa. Clearly, it is of significant importance to understand the origin and extent of the superstrengthening effect in ceramic nanocomposites, and critical experimental and theoretical evidence is needed to verify and understand reported result.

From our extensive density-functional theory calculations for interfaces in this nanocomposite, we find that the favorable structure, formed under the technically relevant nitrogen-rich conditions, involves a single Si layer tetrahedrally coordinated to N atoms sandwiched between TiN(111) crystallites. The tensile strength of bulk TiN in the \(<111>\) direction is found to be notably greater than in the \(<100>\) and \(<110>\) directions, and similar to the weakest bonding direction of diamond. This suggests that the enhanced hardness of the nanocomposites compared to that of its constituent materials, is primarily due to their affording and enhancing predominant interface formation involving the polar TiN(111) planes. We also find that oxygen impurities diffuse to the interface region, forming strong bonds with Ti atoms and inducing a striking reduction in the tensile strength of the interface. Given the found deteriorating effect of oxygen on the tensile strength of the interfaces favorable under nitrogen-rich conditions, this
indicates that oxygen contamination should be avoided in the creation of the nanocomposites if superhard coatings are desired, and could also be responsible for varying reported values of the hardness of this material.

Figure 4: (a) Tensile stress as a function of uniform strain for various systems in various crystallographic directions. (b) Inter-planar stress versus tensile strain applied between atomic layers. The maximum stress corresponds to the theoretical tensile strength of the material (from Ref. [6]).

![Figure 4: Tensile stress vs. strain](image)

For further information see: [http://www.physics.usyd.edu.au/cmt/](http://www.physics.usyd.edu.au/cmt/) or contact Prof. C. Stampfl: stampfl@physics.usyd.edu.au

**Publications since last report**


Figure 5: Atomic structure of various interfaces considered for the "nc-TiN/a-Si_N_y" nanocomposite (from Ref. [4]). Blue, grey, and red spheres denote nitrogen, titanium, and silicon atoms respectively.

![Figure 5: Atomic structure](image)