**IT4Innovations 4th Open Access Call**

To be submitted before: 3.10.2014

**Name of the project: *Ab initio* study of optical properties of amorphous TiO2-based materials  
Number of core hours requested:114000**

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**Research area:** Materials Science, Physics

**Popular abstract:**

Titanium dioxide (TiO2) thin films are extensively studied because of their interesting optical, electrical and chemical properties. TiO2 is a wide band gap semiconductor, hence it is transparent over a wide range of wavelengths. TiO2 has a high refractive index and high static dielectric constant. The optical properties of TiO2 motivate research on applications such as multilayer antireflective coatings, interference filters, or waveguides.

Regardless its exciting properties, the current material quality of TiO2 thin films still limits their performance. Columnar morphology generally observed in TiO2 coatings leads to increased optical losses and degradation of its insulating behavior. It has already been shown that mixing Si-O and Ti-O bonds leads to more homogeneous material (i.e. suppression of the columnar structure of pure TiO2 films) and an increased fraction of amorphous phase. Consequently, controlled implantation of Si into TiO2-based materials is a perspective way how to alter the dielectric constant and refractive index, and simultaneously to improve insulating properties. Additionally, it is anticipated that the material will become transparent for a broader range of wavelengths. Other alloying elements, e.g. Nb or Ta, has been proposed to act similarly to Si.

Modern computational methods allow for a significant reduction of experimental efforts and costs by providing materials trends and selection rules. In particular, quantum-mechanical calculations based on the Density Functional Theory provide highly accurate and affordable predictions. Using available computational power provided by the Anselm supercomputer will enable high throughput calculation approach, which is needed to properly scan a large set of various TiO2-based materials. This will serve as a starting point for subsequent experimental work focused on further application-orientated material development.

**Scientific readiness:**

**Aims and objectives**

The aim of this project is to predict properties of selected Ti1–n*X*nO2 amorphous phases, where the promising candidates for *X* include Si, Zr, Hf, Sc, Nb, Ta, Al or Ge. Special attention will be paid to optical-related properties such as the band gap or the dielectric function. Amorphous unit cells for various concentrations *n* ranging from 0 to 1 will be constructed, structurally optimized, and their properties will be calculated and evaluated. Broad scope of this study, allowed by the available computational power, will enable thorough probing of the amorphous materials and to identify concentration related trends. The present proposal is a follow up project of an ongoing project “Optical properties of TiO2 based alloys from first principle calculations” (Anselm project OPEN-3-9), within which we are building a “materials library” of Ti1–nXnO2 solid solutions. This proposal will enable to extend our systematic materials search also to amorphous structures.

**Methods and state-of-the-art**

Ti1-n*X*nO2 amorphous materials will be modeled using a supercell-based *ab initio* Molecular Dynamics approach (“simulated annealing”) (amorphous unit cell generation and structural optimizations will be done using co-investigater’s computational resources). The cell sizes will be in a range of around 100 atoms as a compromise between having an “infinite” amorphous cell and making the study computationally feasible. The quantum mechanical calculations will be performed within the framework of Density Functional Theory (DFT) [2,3], which replaces a solution of the Schrödinger equation for many-body wave-function with a search for charge density. An all-electron fully relativistic DFT package WIEN2k will be used in this project. It is based on the full-potential (linearized) augmented plane-waves + local orbitals method [4], one among the most accurate schemes for band structure calculations. It has implemented recently developed modified Becke-Johnson (mBJ) exchange-correlation potential which yields highly accurate energy band gaps for most semiconductors and insulators, with experimental agreement of the same order as much more computationally expansive hybrid functional or GW methods [5].

**Impact and outlooks**

While there are multiple works concerning experimental properties of doped Ti1-n*X*nO2 [e.g., 6, 7, 8] both in amorphous and crystalline phase, most *ab initio* studies are limited to investigations of low concentration doping of anatase and rutile TiO2 structures [e.g., 9, 10, 11]. Only few works report on calculated properties of amorphous TiO2 or Ti1-n*X*nO2 mixtures [e.g., 12, 13], however none of those focused on optical properties.

This project aims to fill this gap by studying compositional trends in Ti1-n*X*nO2 amorphous materials, with a strong focus on the band gaps and optical properties and will enhance the “materials library” built as a part of preceding (currently running) project OPEN-3-9. Such database will allow a thorough analysis of alloying related material properties and selection of the best candidates for further experimental studies and applications.

When combined with the OPEN-3-9 project results, we will be able to predict preferred material structure (anatase, rutile, amorphous, etc.) as a function of concentration *n* of the dopant *X*.

Calculated optical properties together with the underlying band structure will also help to better understand the nature of electronic transitions in these materials, hence facilitating a development of advanced dispersion models. Such models are important for routine and accurate evaluation of optical measurements and characterization of experimental samples.

**Computational readiness:**

**Computational approach, parallelization and scalability:**

WIEN2k software used for this project is written in FORTRAN90 and requires a UNIX system (programs are linked together via C-shell scripts). The applicant owns a valid academic license. WIEN2k does not require any special libraries, but it uses optimized BLAS and LAPACK libraries if present. It is mostly tested and optimized for the Intel proprietary compiler, but can be built with GNU compiler collection as well.

WIEN2k has a built-in parallelization scheme (so-called k-point parallelization), where subsets of the k-point mesh (sampling the Brillouin zone) are distributed to different processors, and subsequently combined. There are some parts of the main self-consistent file (SCF) cycle which are not parallelized, however their computational costs are negligible compared with the rest of the cycle.

Additionally, MPI fine-grained parallelization can be used when necessary, e.g., for memory limited problems or where there are fewer k-points than available processors.

One typical SCF cycle on a test 96-atom amorphous unit cell takes approximately 40 CPU-hours, out of which only about 12 minutes are pure serial code, and the rest makes use of the built-in k-point parallelization scheme.

**Computational resources:**

Requested resources were estimated from older computation of amorphous unit cell with 96 atoms cell size and 3x3x3 k-points grid done on Anselm cluster as a part of project OPEN-3-9.

Planned amount of calculated structures: 30  
Usual number of SCF cycles needed to converge a calculation using the mBJ potential: 60-80  
Core hours needed for one typical cycle with 96 atoms cell size: 40  
Additional core hours needed for larger test cases (to test cell-size effects) and for post-processing analysis: 30000

Total CPU hours needed: 30 \* 70 \* 40 + 30000 = 114000

**Socioeconomic impact:**

In a long run, this research could lead to a development of novel components such as multilayer antireflecive coatings, interference filters, or waveguides with greatly improved optical performance.

Outside of optical application, another widespread use for TiO2 and Ti1-nXnO2 oxides is in photocatalysis, with applications including self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, and photoelectrochemical conversion.

**Operational costs:**

This work will be done in parallel to experimental studies performed within the frameworks of funded projects of the CEITEC Plasma Technologies group (group leader Prof. Lenka Zajíčková). The calculations will be done within the PhD project of Pavel Ondračka (principal investigator of this proposal), whose scholarship is paid from the Masaryk University and CEITEC resources. There are no other financial resources available for the PI to cover the operational costs related to the use of the supercomputer.

**Amortization and renewal:**

As described above, there are unfortunately no free financial resources available towards amortization and renewal of the cluster hardware.

**References:**

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1. Comma separated list [↑](#footnote-ref-2)