TiO_2 functionalization by N-ion implantation

A theoretical DFT study

Antonio M. Márquez

Departamento de Química Física
Universidad de Sevilla, Spain

JIS 2010, Braga

Objective of surface functionalization

FUNCOAT
SURFACE FUNCTIONALISATION OF MATERIALS FOR HIGH ADDED VALUE APPLICATIONS

Scientific and technological objectives are:

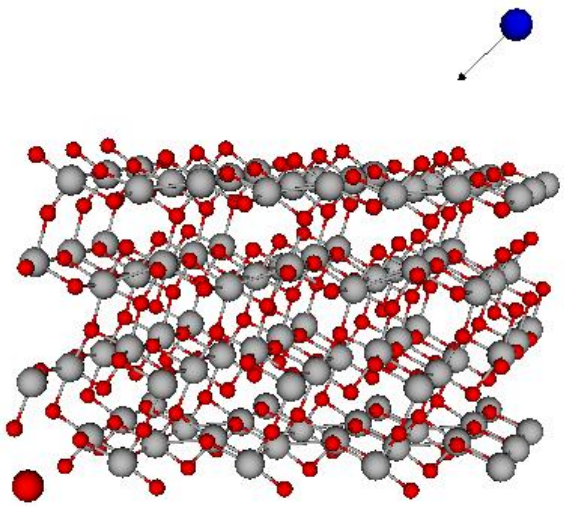
- understanding of fundamental phenomena driving the modification of surfaces and interfaces
- control of the micro- and nano- structure of surfaces and thin films, and the optimization of thin film deposition methods
- process development of multifunctional surfaces for novel applications (mechanical and metallurgical, optical, magnetic, energy, biomaterials, . . .)
- production of new devices based on functionalised surfaces

Plasma interaction with surfaces

- Many surface activation procedures and thin film techniques are based on the use of plasmas
- Understanding of the plasma physics and chemistry is essential to predict the properties of functionalized surfaces
- Objectives:
  - Identification of plasma species
  - Determination of parameters (particle energy, excited species, chemical changes at surfaces, ...)
  - Predict the effect of the interaction of these plasmas with the surfaces

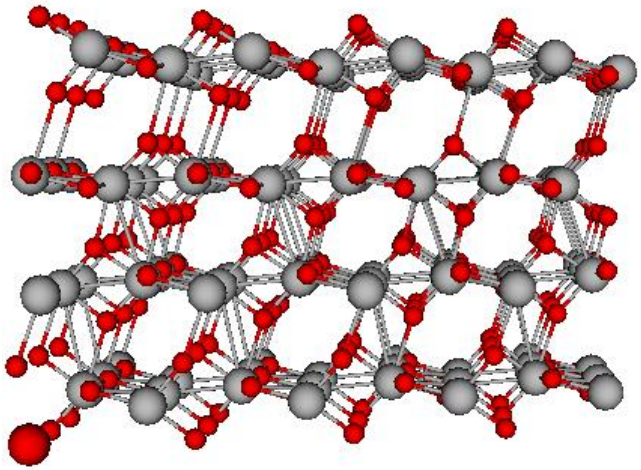
Molecular Dynamics Model

- Study the implantation of nitrogen atoms into the TiO_2 network
- Simulate the process by etching the TiO_2 surface with N atoms with kinetic energies in the $10 - 100$ eV range
- N atoms impinging the surface with a constant $45°$ angle at random positions (6 different shots)



Surface Model Details

- 3×4 supercell model of a TiO_2-anatase (101) surface with four O-Ti-O layers (288 atoms, $\simeq$ 1500 e^-)
- surface area $\simeq 24$ $Å^2$
- Density Functional Theory (GGA-PW91) calculations
- Plane Wave basis functions using a 300 eV cutoff ($\simeq$ 550000 plane waves)

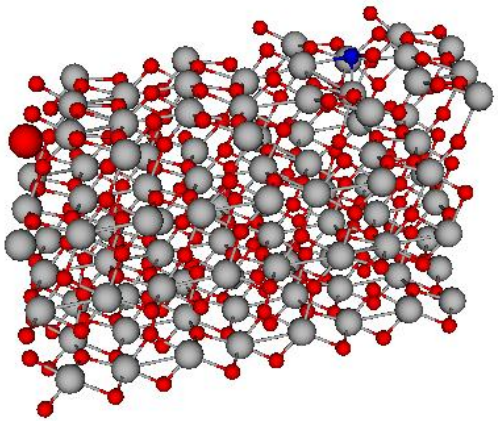


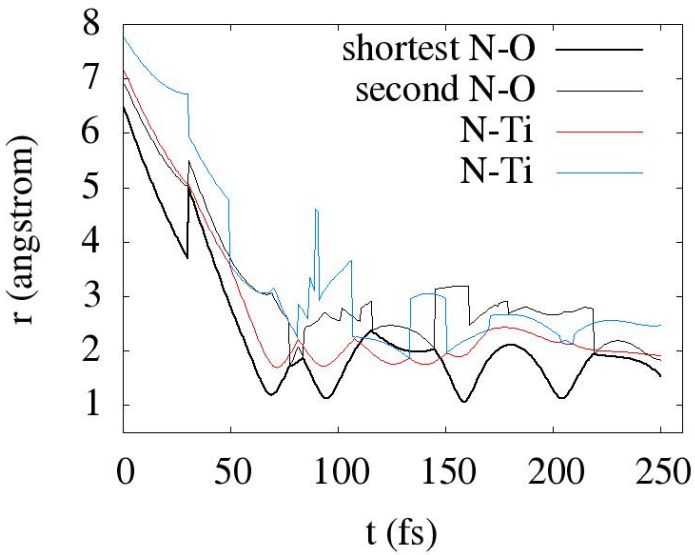
Molecular Dynamics Details

- *ab initio* molecular dynamics from DFT calculation of the wavefunction and forces at each MD step
- Surface pre-equilibrated a $298\ \mathrm{K}$
- NVE simulation (microcanonical ensemble) to avoid artificial cooling of the impinging atom before reaching the surface
- Simulation time step $0.5\ \mathrm{fs}$
- Total simulation time $0.25\ \mathrm{ps}$
- Wall time $\simeq$ 5-7 days per calculation (16-24 cores)

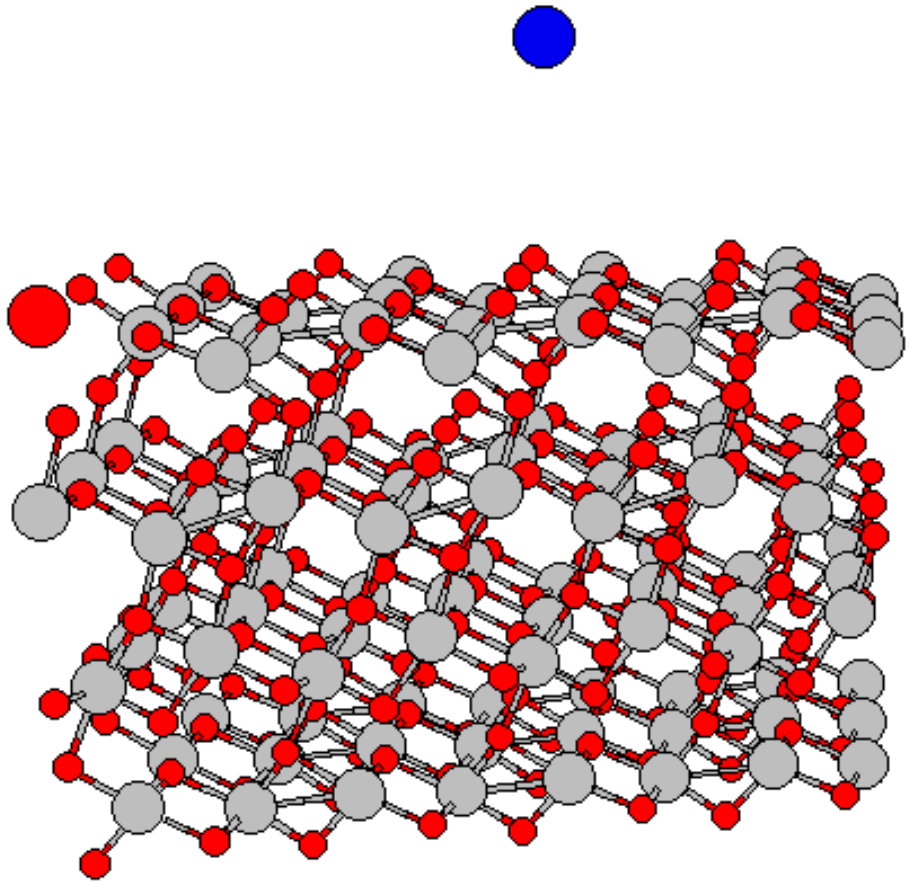
Low Energy ions (KE=10 eV)

- No N ions incorporated into the TiO_2 subsurface
- No apreciable surface etching
- Formation of surface NO molecules



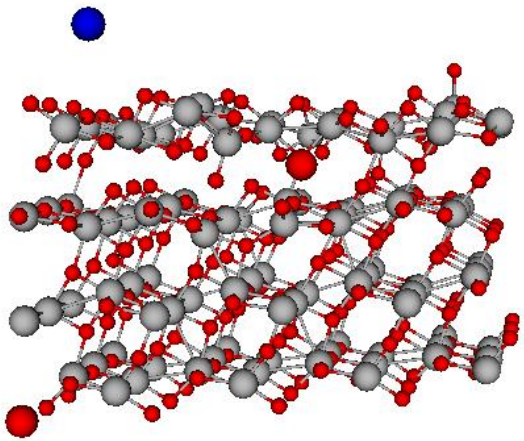


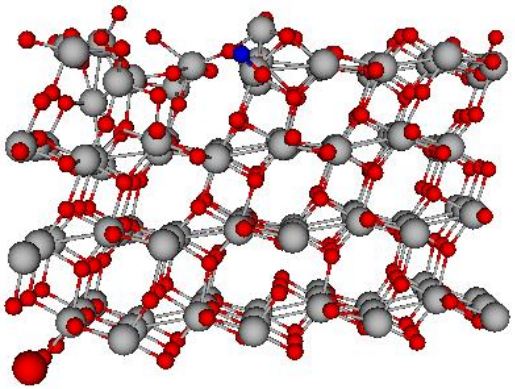
Simulation at KE=10 eV



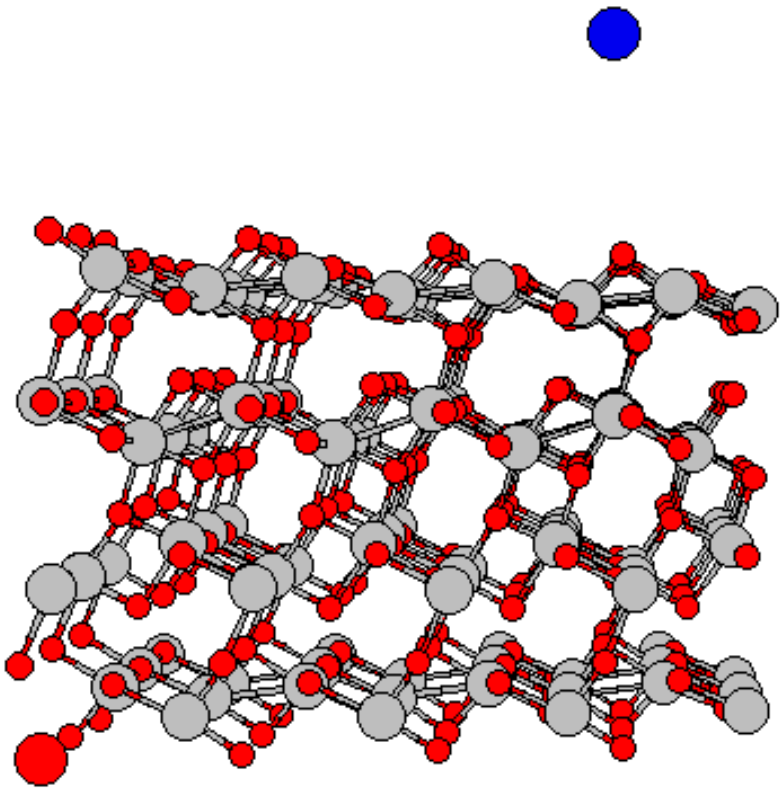
High Energy ions (KE=50 eV)

- The impinging N ion usually penetrates the surface (ocassionally up to the third O-Ti-O layer)
- Creation of defects: Ti and O interstitials
- a large disruption of the surface is created
- Model may be inadequate !!!



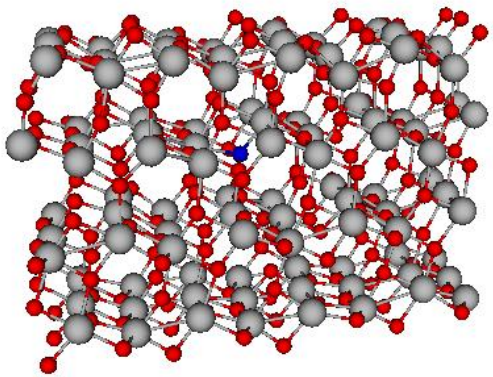


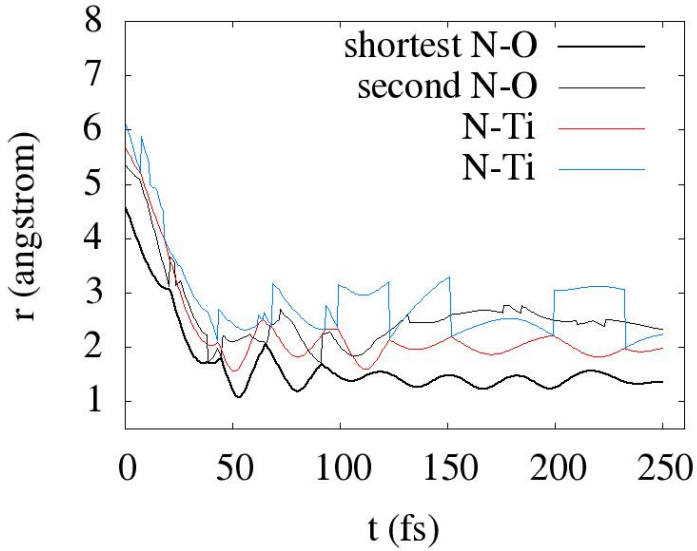
Simulation at KE=50 eV



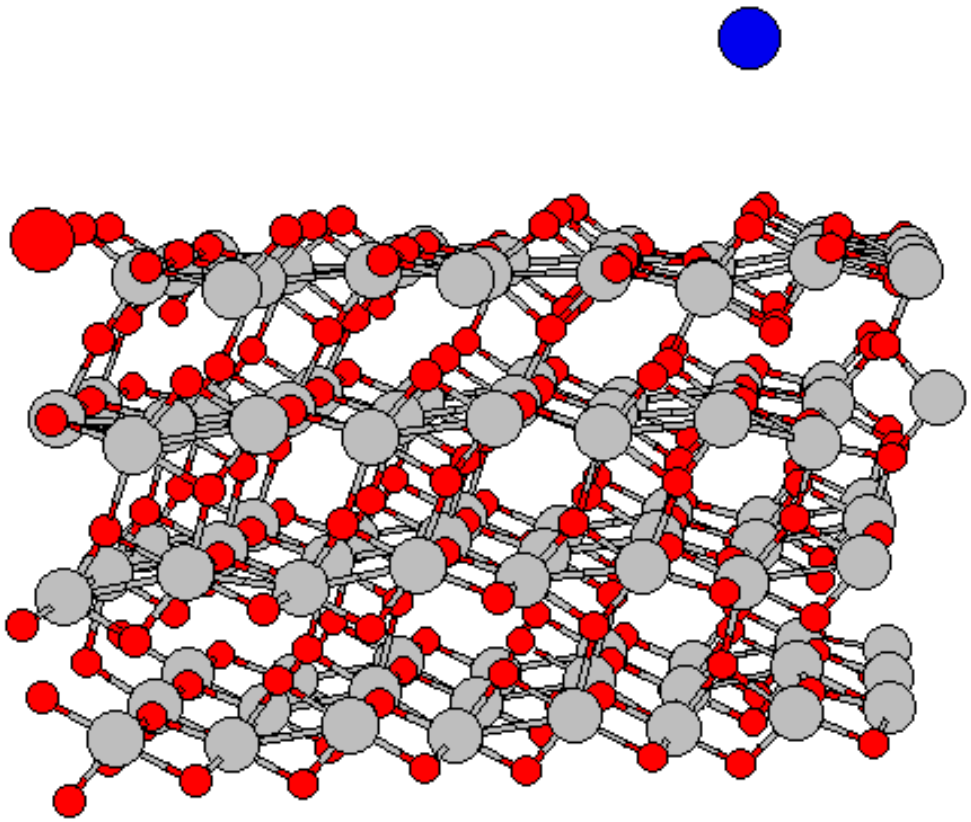
Medium Energy ions (KE=20 eV)

- Lower surface disruption (model is adequate)
- N incorporation into the subsurface
- formation of interstitials
- NO formation is usual
  - implies surface reduction
  - may explain voids found experimentally





Simulation at KE=20 eV



Conclusions

- Model adequate to study ion implantation by low-temperature ion beams (up to $KE \simeq 50$ eV)
- Simulations prove to be useful means of
  - understanding fundamental phenomena driving the modification of surfaces and interfaces,
  - understanding plasma physics and chemistry
  - determination of main parameters: *particle energies*, *chemical changes at surfaces*, ...

Future work

- Increase number of N ions in the simulations
- Analyze formation of new TiO_2 or $TiO_{2-x}N_x$ phases
- Study the evolution of the surface on longer time scales

Acknowledgements

Colaborators

- J. Fernández Sanz (U. Sevilla)
- Agustín Rodríguez González-Elipe (CSIC - Sevilla)

Funding

GOBIERNO DE ESPAÑA MINISTERIO DE EDUCACIÓN

Spanish MEC: project CSD2008-00023

FUNCOAT
SURFACE FUNCTIONALISATION OF MATERIALS FOR HIGH ADDED VALUE APPLICATIONS

CICA
JUNTA DE ANDALUCIA

Computer Time

Thank you !