Electronic structure of N doped Anatase TiO_2

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BROOKHAVEN NATIONAL LABORATORY

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Overview

- ✓ Why TiO_2
- ✓ Synthesis of N doped TiO_2
- ✓ HAXPES
- ✓ Electronic structure of N doped TiO_2
- ✓ Conclusions

Why TiO_2

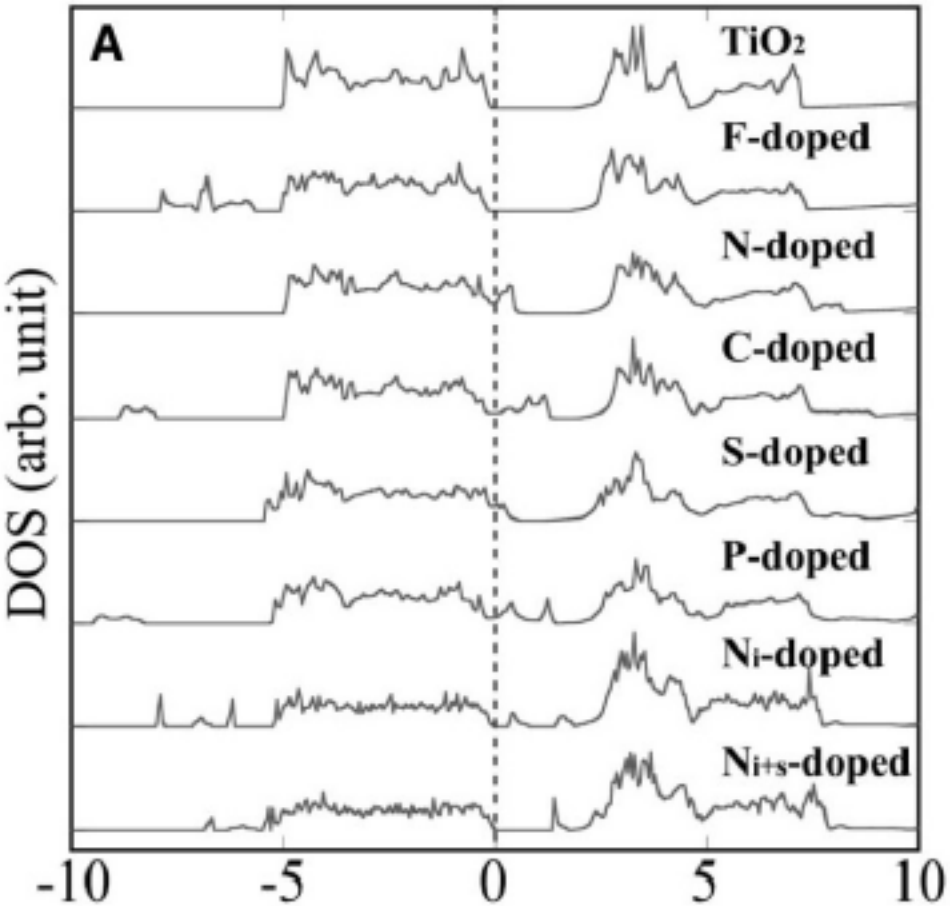
Properties

- ✓ TiO_2 is a wide band gap (3.2eV) semiconductor
- ✓ High refractive index
- ✓ High dielectric constant
- ✓ Large thermo power
- ✓ High n-type mobility

Applications

- ✓ Photocatalysis
- ✓ Photovoltaic solar cells
- ✓ Photolysis of water

Doped TiO_2



N doped synthesis

Ion Implantation: A. Nambu et al.

J. Chem. Phys. 125, 094706 (2006)

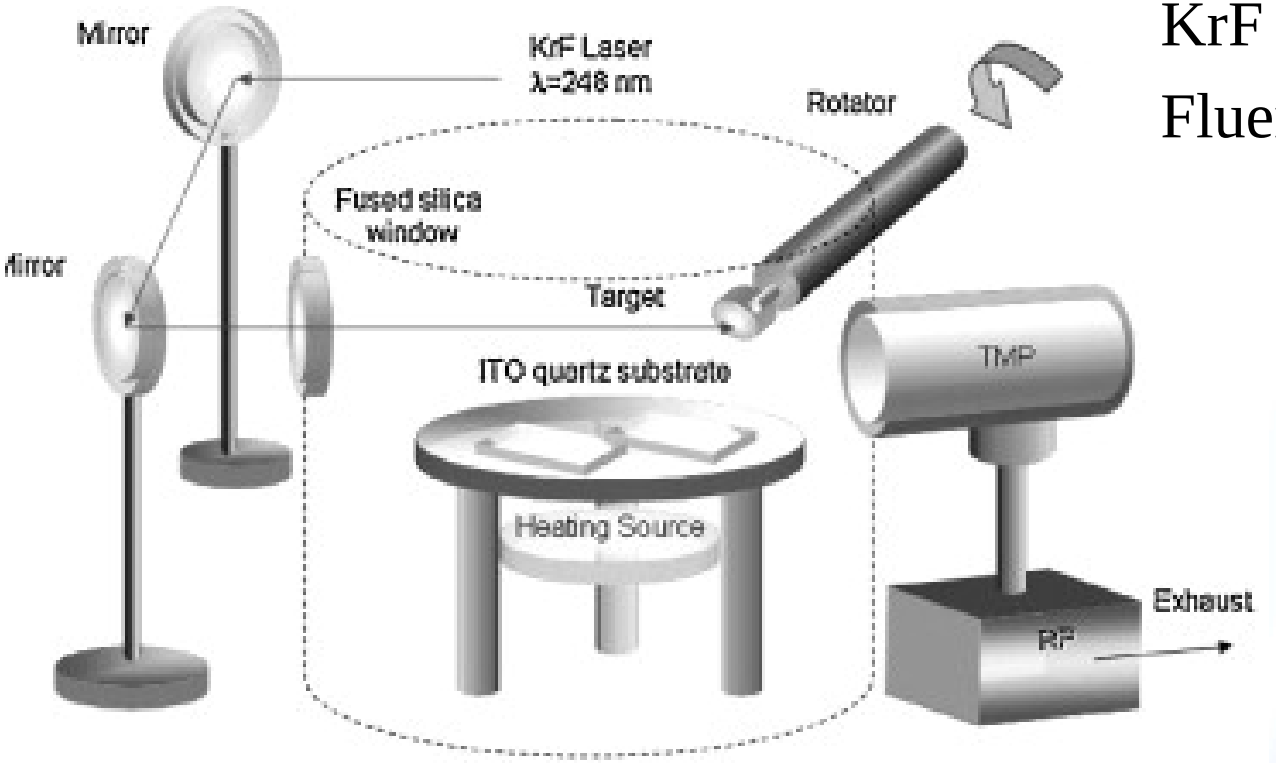
Plasma MOCVD: S. Buzby et al.

J. Vac. Sci B, 24 1210 (2006)

Chemical Routes: K. Kobayakawa et al., J. Photochem. Photobiol. A, 170, 177 (2005)

Asahi R, Morikawa, T., Ohwaki, T., Aoki, K., and Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. **Science** 2001;293(5528):269-71

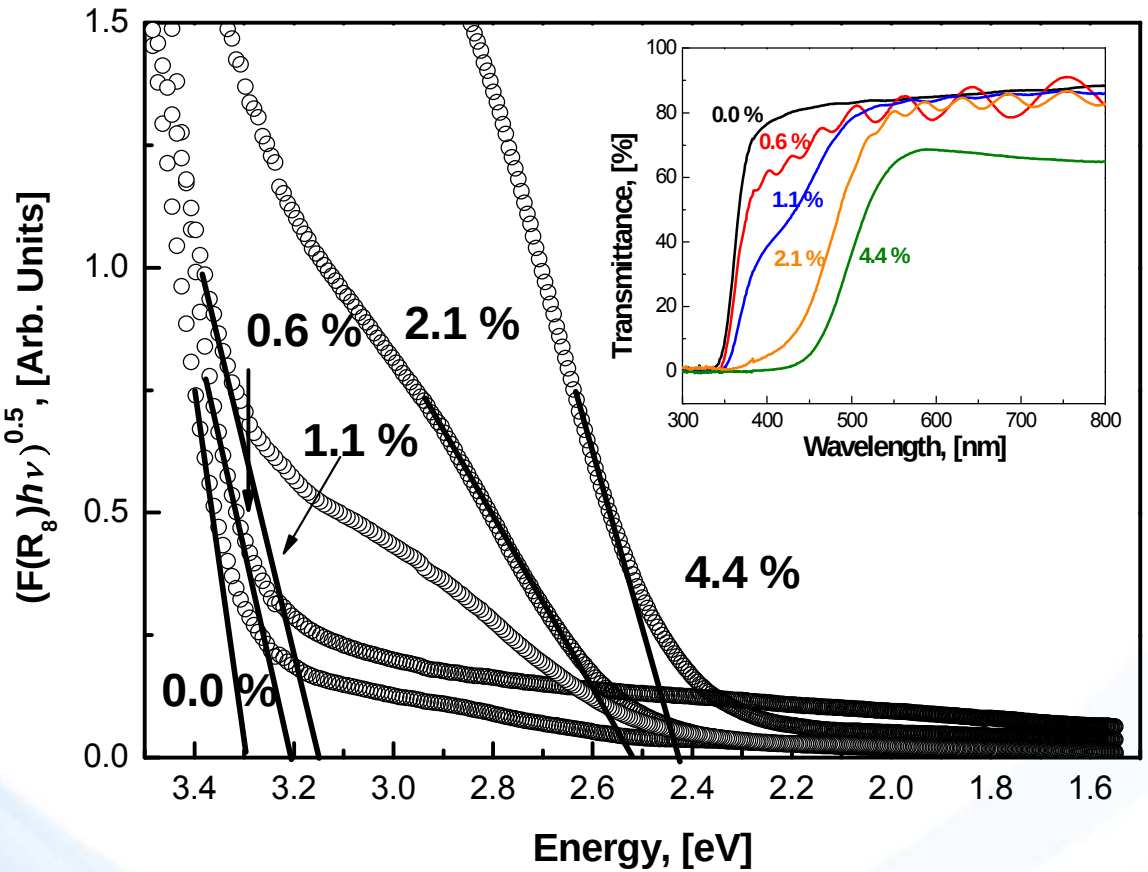
Reactive Pulsed Laser Deposition



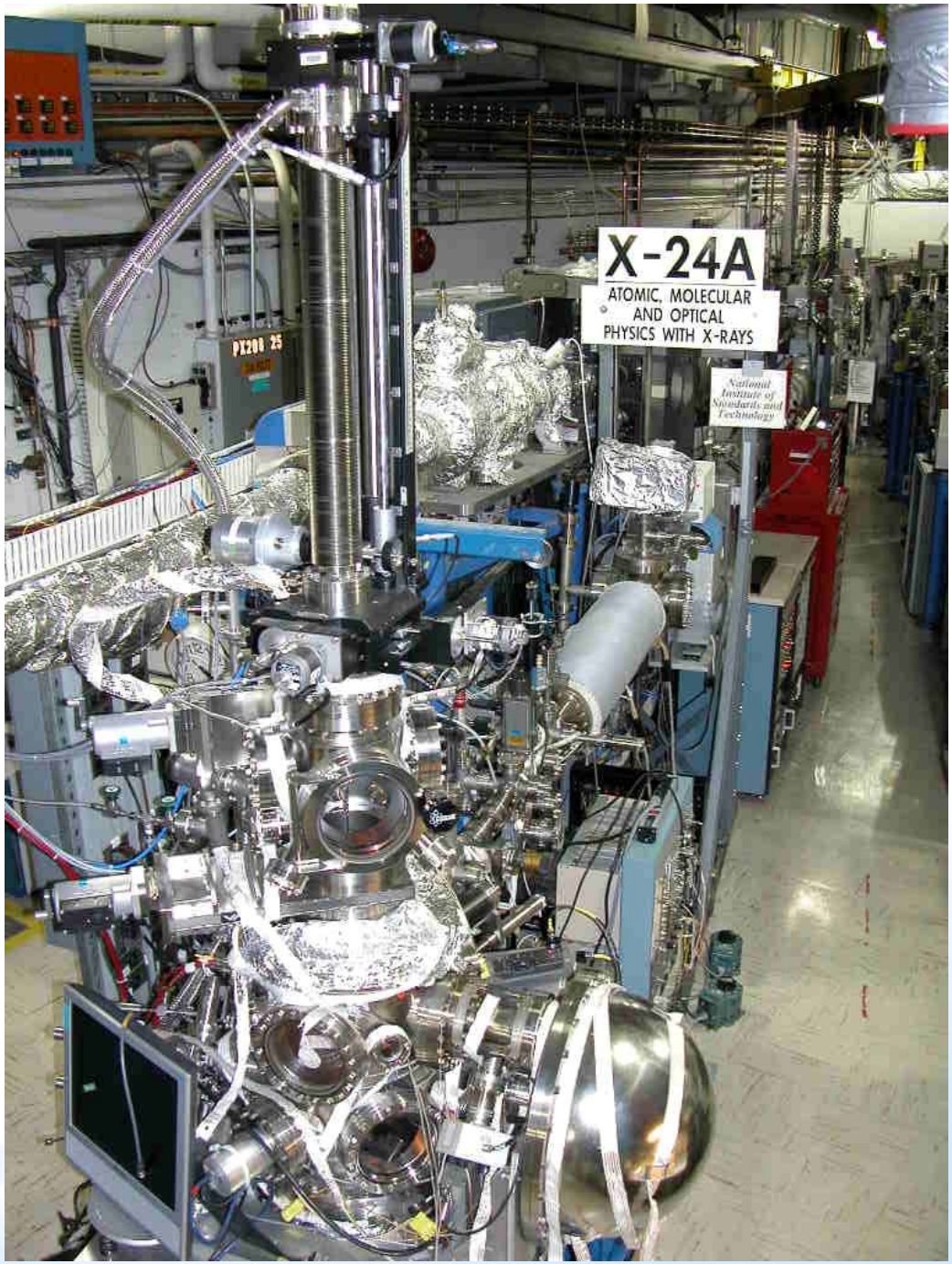
KrF Laser (248 nm)

Fluence <2 J/sq. cm

Band Gap Measurement



The approximated indirect band gap obtained using the transformed Kubelka-Monk function.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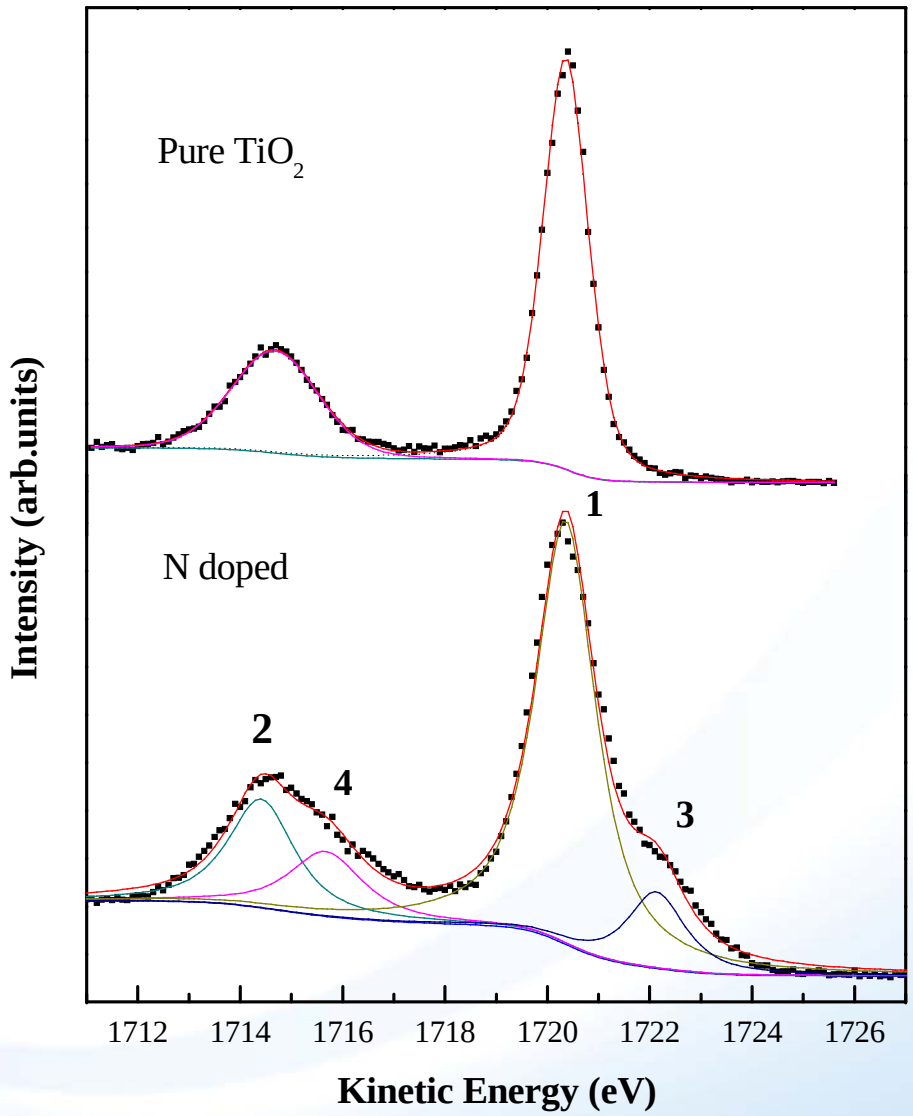
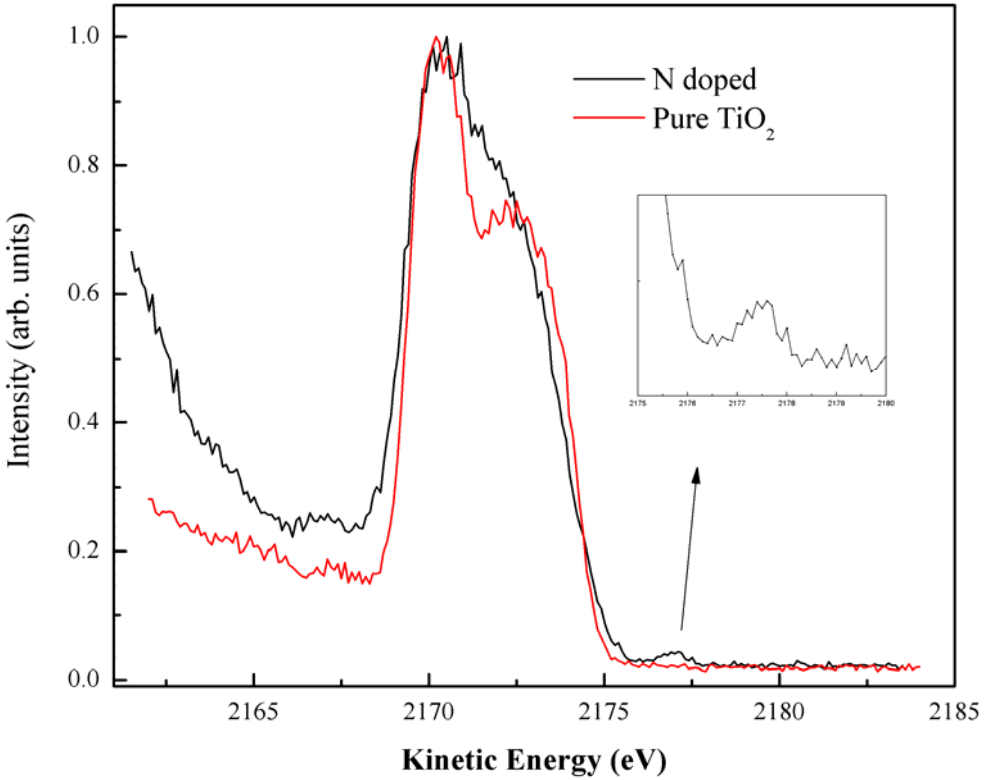
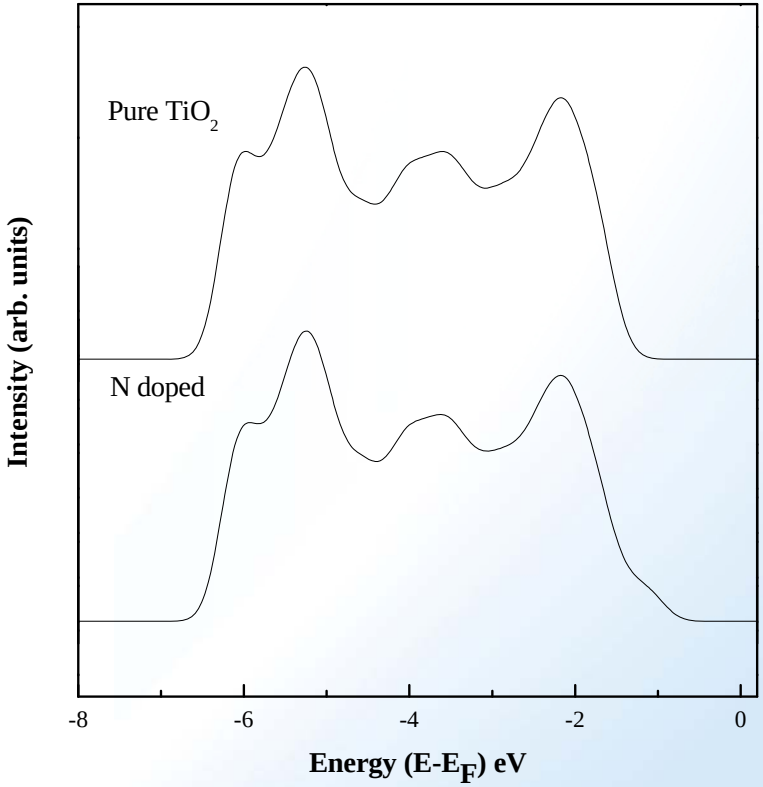
XPS Core Level

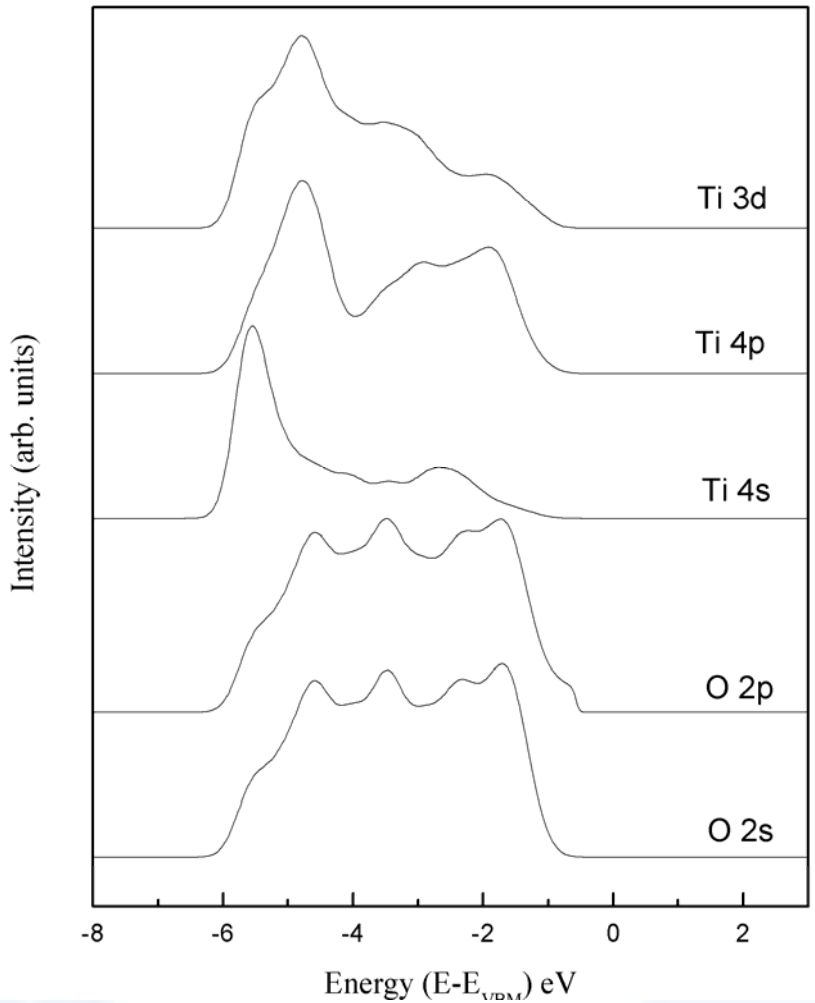


Valence Band





Angular momentum resolved par. DOS



Theoretical Atomic Cross Sections

Trzhaskovskaya, V. I. Nefedov, and V. G. Yarzhemsky, At. Data Nucl. Data Tables **77**, 97 (2001).

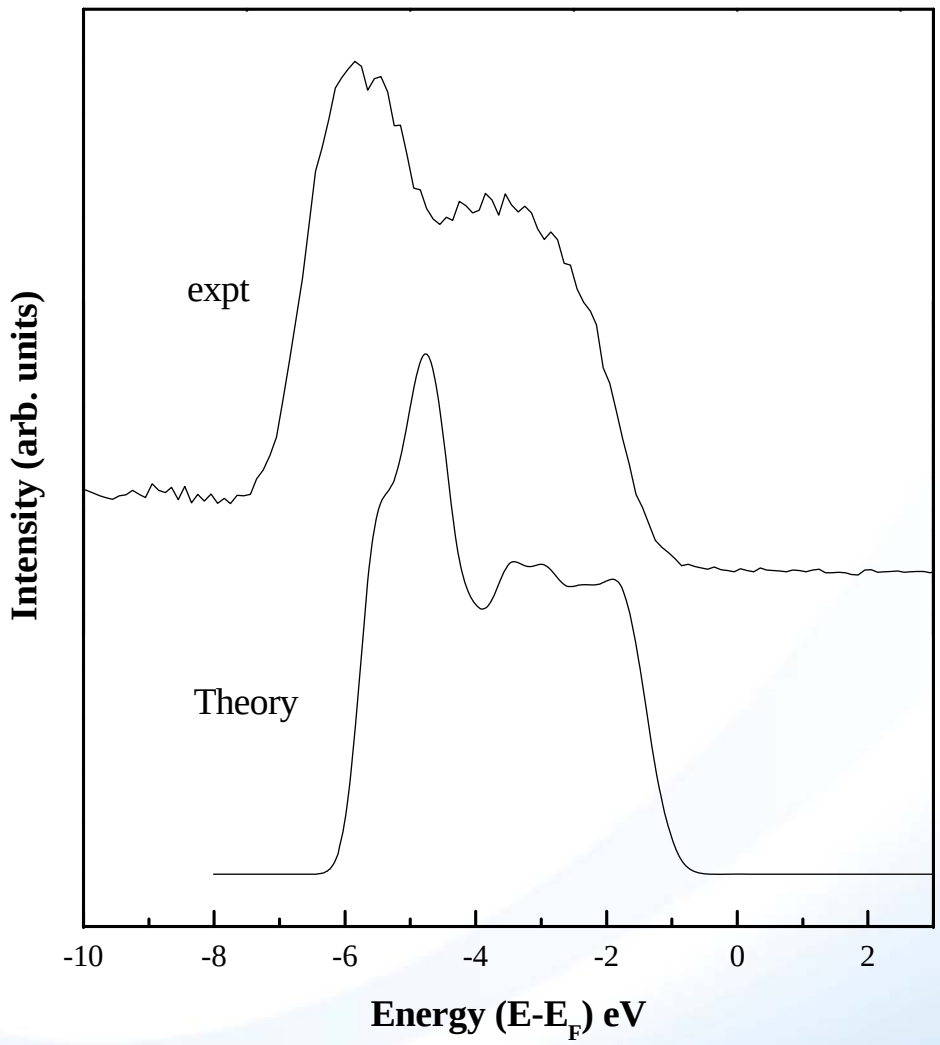
$$\frac{\sigma_{Ti_{4s}}}{\sigma_{Ti_{3d}}} \approx 2.3\ !$$

$$\frac{\sigma_{O_{2s}}}{\sigma_{O_{2p}}} \approx 9.8\ !$$

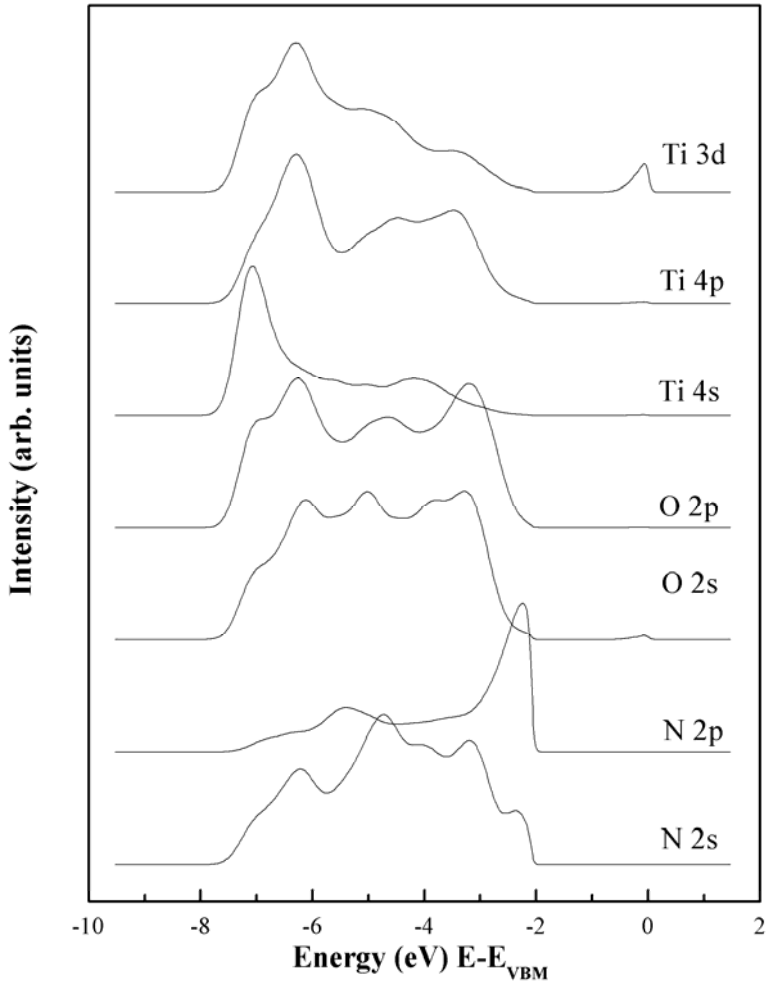
$$I(E,\hbar\omega)\ \alpha\ \sum_{i,l} \rho_{i,l}(E)\ \sigma_{i,l}(E,\hbar\omega)$$

J.C. Woicik et al. PRL, 89, 077401 (2002)

VB Theory & Experiment



Angular momentum resolved par. DOS



Theoretical Atomic Cross Sections

$$\frac{\sigma_{Ti_{4s}}}{\sigma_{Ti_{3d}}} \approx 2.3\ !$$

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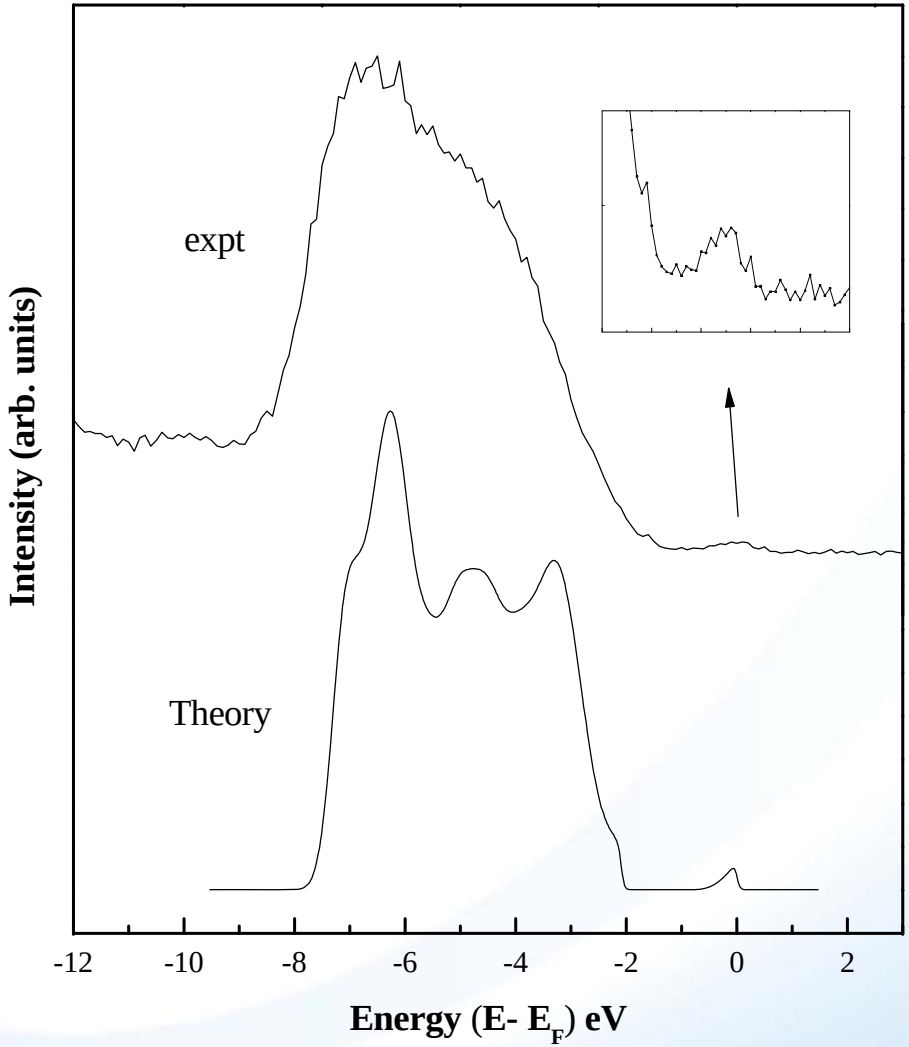
$$\frac{\sigma_{N_{2s}}}{\sigma_{N_{2p}}} \approx 13.6\ !$$

VB Theory & Experiment: N doped TiO_2



Conclusions

- N doped TiO_2 synthesized via reactive PLD
- UV-vis shows BG reductions
- VB spectra shows oxygen vacancy related level.
- Comparison of VB with calculations reveal hybridization between different states

Acknowledgements

- Dr. Joseph Woicik (NIST)
- Dr. E. Cockayne (NIST)
- Dr. H.Y.Lin (Intel)
- Dr. S.I.Shah (U. Delaware)
- Dr. D.P. Siddons (NSLS)