Nanocrystalline heterophase boundaries and asymmetric topographies for enhanced photocatalysts produced by dual ion beam-assisted deposition

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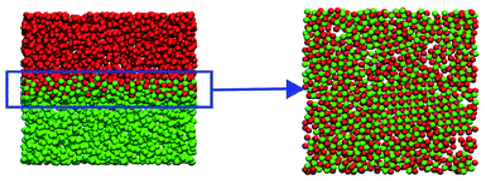
ABSTRACT

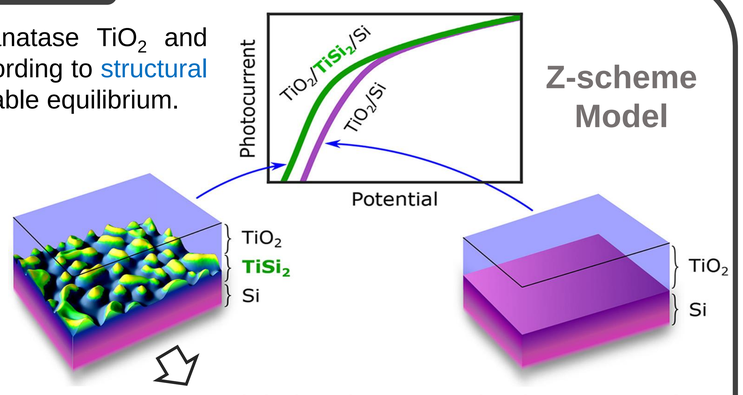
The development of **functional interface-based assemblies** is urgently needed to meet global energy sustainability standards. All of those technological advances and breakthroughs in the fabrication of ***z*-scheme photocatalysts systems**, involving the synthesis of different polymorphs and metastable inorganic solids, are still challenging. From the **combinatorial experiments** (*bottom-up* and *top-down*), it is possible the **hybrid-structure integration** that has been actively exploited as a promising alternative to enhance the benefits in micro- and nanotechnologies. Particularly, thin film deposition of **nanocrystalline transition metal oxides and silicides** (e.g., TiO_2 and $TiSi_2$) is a pattern of resource use that aims to achieve high-performance (opto)electronic devices.

HETEROPHASE JUNCTIONS (HPJs)

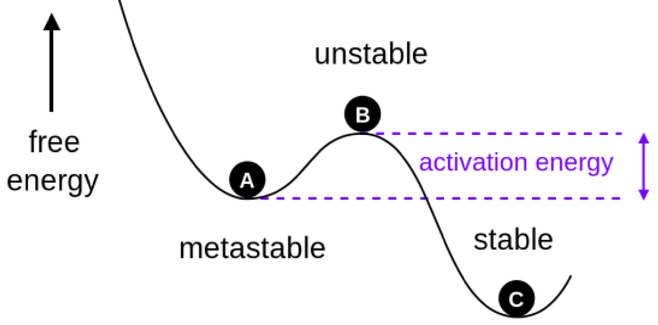
❑ **Metastable inorganic materials** (anatase TiO_2 and $TiSi_2$ semiconductors**)** are classified according to structural variety and energetic departures from stable equilibrium.

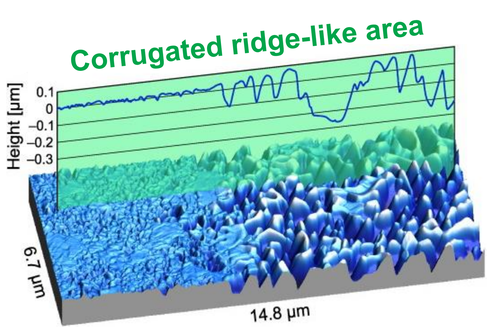


Complex mixed-phase interface system



Modulating the properties by means of atomic-level defect engineering





Expected achievements:

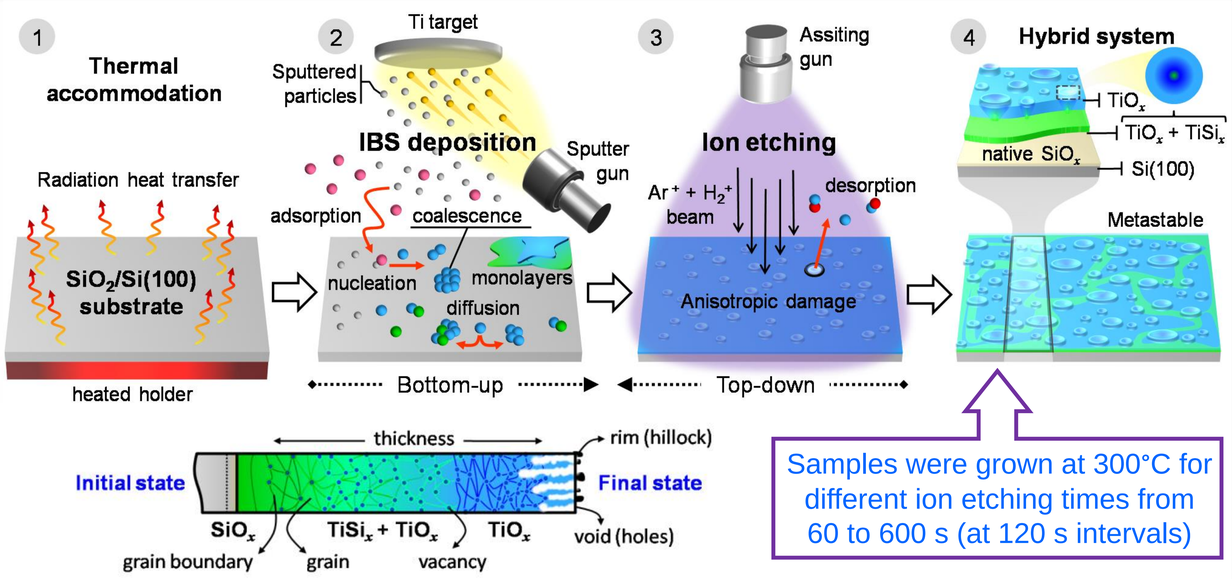
(1) **Chemical intermingling** of (Ti, Si)O and Ti-Si (heterophase) formed at the film-substrate interface.

(2) Design of **nanohole structures** produced by *in situ* normal-incidence ion irradiation (~ 0.4 keV Kaufman cell).

(3) Synergistic effect of **ion sputter-etching** (self-reduction & surface functionalization).

EXPERIMENTAL METHODS

Fabrication of nano-sized films (≤ 50 nm thick) induced by dual ion beam assisted deposition



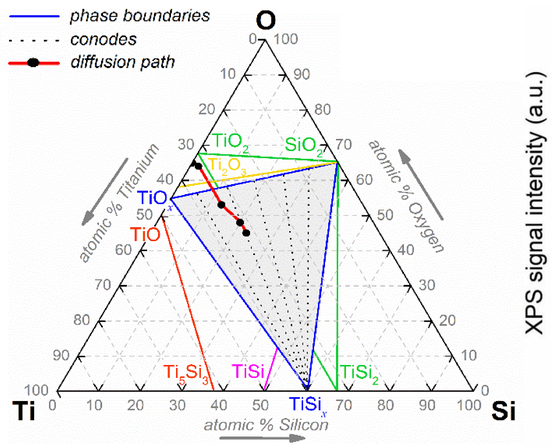
Samples were grown at 300°C for different ion etching times from 60 to 600 s (at 120 s intervals)

Low-energy ion beam · Film-forming particles · Reactive gases · Titanium oxide · Titanium silicide

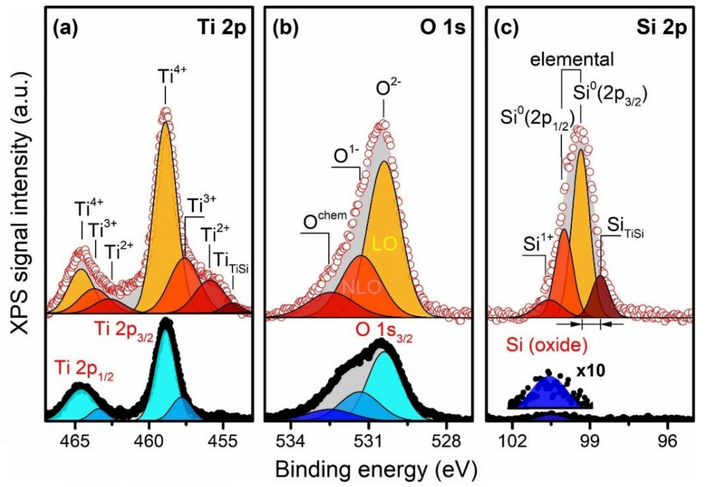
↓ Direct ion acceleration · O Localized material removal · Volatile species · Cavities

KEY RESULTS ON Ti-BASED METASTABLE NANOFILMS

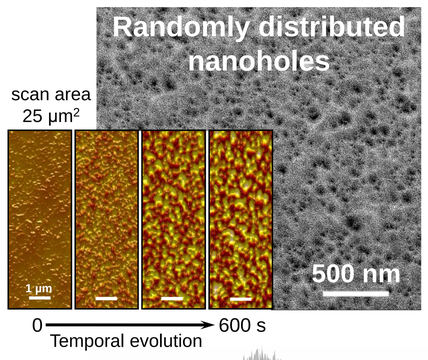
Ternary phase diagram

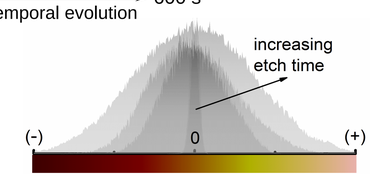


(i) Chemical bonding states and surface composition

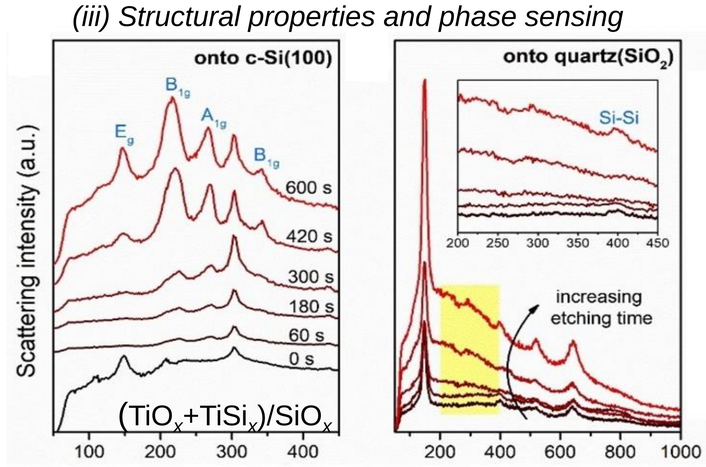


(ii) Surface (topographic) morphology

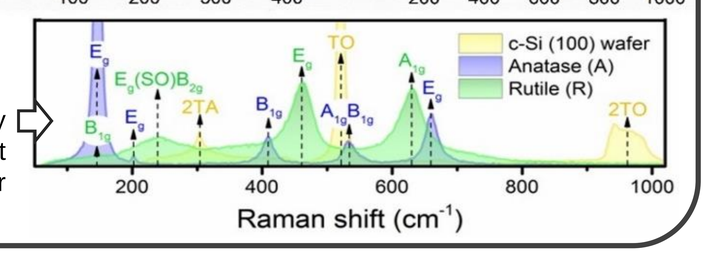




(iii) Structural properties and phase sensing



Raman spectra changes reveal (a)symmetry related to the number (and activity) of different vibrational groups and structural (dis)order induced by surface erosion.



SUMMARY

❑ Photoactive top anatase TiO_x sub-oxide nanofilms related to **(Ti/Si):O hybrid interface** (with variable stoichiometry ratios).

❑ Surface restructuring produce **nanohole patterns** by domain ordering kinetics, relative thermodynamics stability, and removal-relocation mechanisms.

❑ Scenario of **interphase boundaries** and tetragonal-orthorhombic **nanocrystalline**

❑ An inherently non-linear effect caused by temporal evolution of ion erosion, leading to the formation of asymmetric topographies.