# Study of optical and transport properties of nitrogen doped titanium dioxide thin films

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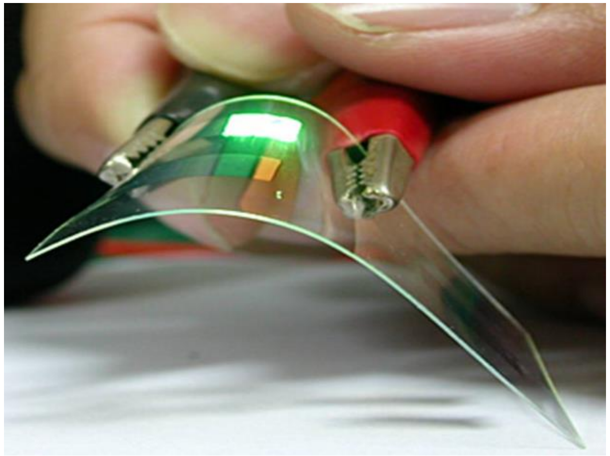
# Introduction

Transparent Conducting Electrodes are part of many technological devices.



Each application has is own challenges and demands.

K. Elmer, *Nature Photonics* **6**, 809 (2012).

# Properties of common TCO

| | AZO | ITO | FTO | TNO (Nb:$TiO_2$) |
|---|---|---|---|---|
| Resistivity (Ωcm) | $2\text{-}3.10^{-4}$ | $1\text{-}2.10^{-4}$ | $8.10^{-4}$ | $9.\ 10^{-4}$ |
| Bandgap (eV) | 3,3 | 3,7 | 3,7 | 3,4 |
| Light Transmission (%) | 85 | 85 | 80 | 75 |
| Cost | Low | High | Low | Low |
| Stability | 3° | 2° | 1° | ? |

$TiO_2$ is interesting because it is not toxic, has high chemical stability, high corrosion resistance, is cheap and many growth routes are well stablished.


T. Minami, *Semicond. Sci. Technol.*, **20** (2005), pp. S35–S44

A. Muthukumar *et. al.*, *Thin Solid Films* **545** (2013), 302-309

N. Yamada *et. al.*, *Thin Solid Films* **516** (2008), 5754-5757

H. Lemire *et. al.*, *Proceedings of SPIE* (2013), 882502

T. Minami *el. al.*, *Journal of Vacuum Science & Technology A* **17** (1999), 1822

# Doping $TiO_2$

| | $Nb:TiO_2$ | $Ta:TiO_2$ | $W:TiO_2$ | $N:TiO_2$ |
|---|---|---|---|---|
| Resistivity (Ωcm) | $9.\ 10^{-4}$ | $2{,}5.10^{-4}$ | $2.10^{-3}$ | $2.10^{-1}$ |
| Visible Light Transmission (%) | 75 | 95 | 90 | 65 |

Anion doping with **Nitrogen** is interesting, but results are behind others.

This poor performance of $N:TiO_2$ may be due to problems to control the crystallinity of $TiO_2$ film under doping by reactive sputtering.


N. Yamada *et. al.*, *Thin Solid Films* **516** (2008), 5754-5757

T. Hitosugi *et. al.*, *Japanese Journal of Applied Physics*, **44** (2005), pp L1063-L1065

U. Takeuchi *et. al.*, *Journal of Applied Physics*, **107** (2010), 023705

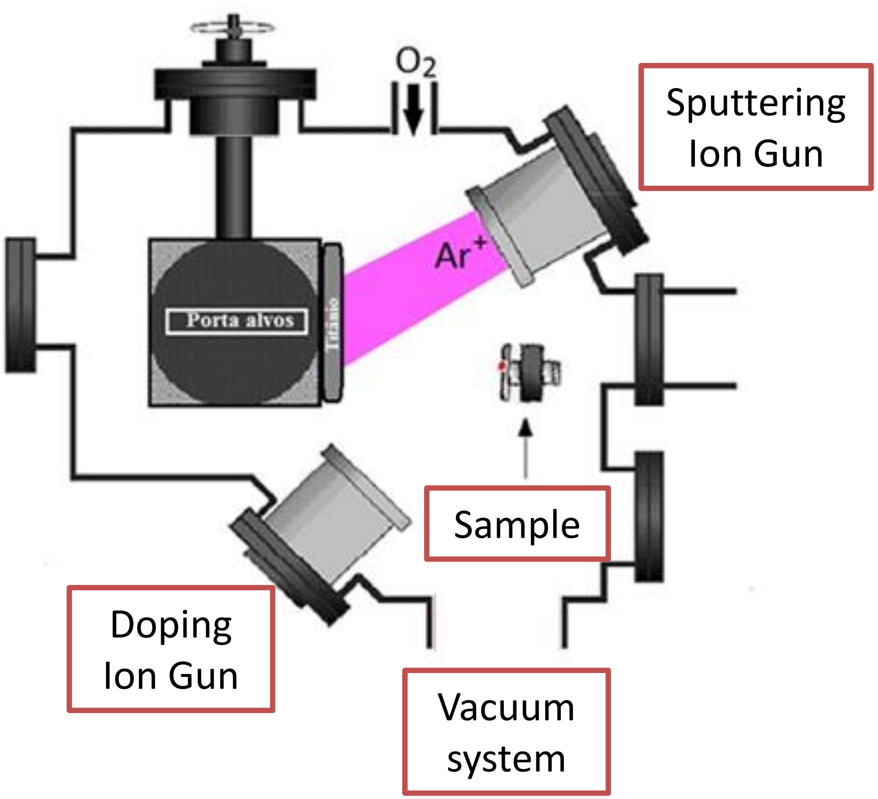
H. Akazawa, *Japanese Journal of Applied Physics*, **49** (2010), 080215T

# Objective

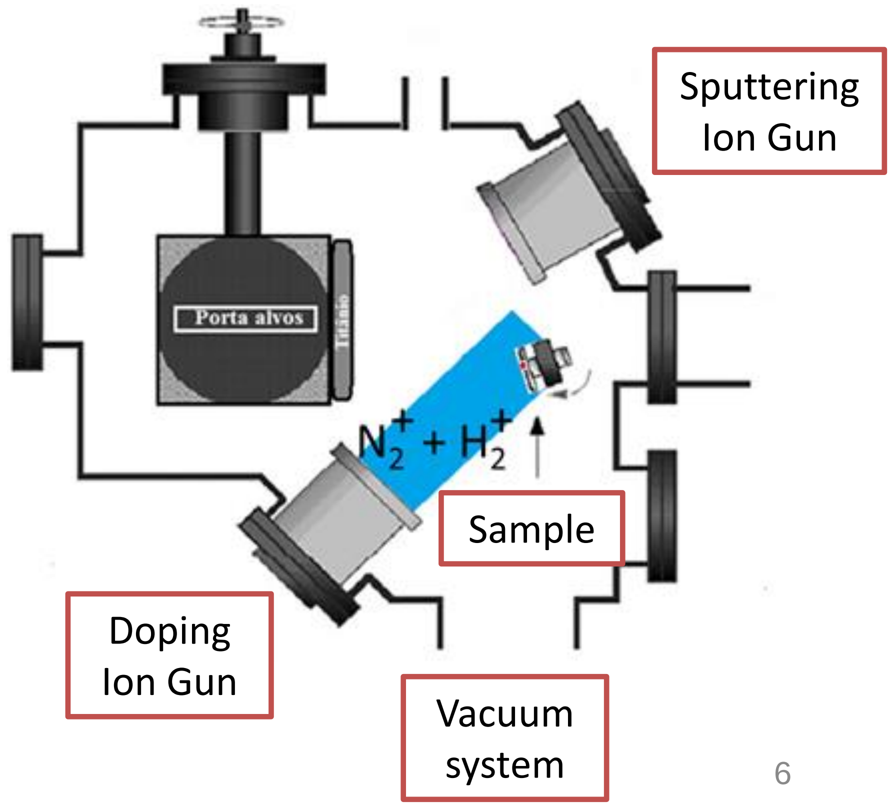
Here, we have grown *undoped* (*in principle* stoichiometric) Anatase $TiO_2$ thin films by reactive sputtering. In a second step, the films were doped by low energy ion implantation and inward thermal diffusion.

# Growth System

Step 1:
Deposition of Anatase $TiO_2$ by Ti target sputtering under $O_2$ atmosphere.




Step 2:
Doping by 400eV $N^+$ and $H^+$ ions.



# Sample preparation settings

## Growth parameters

| Fixed settings for all samples | |
|---|---|
| $P_{O_2}$ | 25 mPa |
| $P_{Ar}$ | 10 mPa |
| $Ar^+$Current density | 8 mA/cm² |
| $Ar^+$beam energy | 1500 eV |
| Deposition time | 50 min |

| Setting changed among samples | |
|---|---|
| Deposition temperature | 400, 500 [°C] |

## Doping parameters

| Fixed settings for all samples | |
|---|---|
| $P_{N_2}$ | 21 mPa |
| $P_{H_2}$ | 2,1 mPa |
| Current density $N_2^+ + H_2^+$ | 1,2 mA/cm² |
| Beam energy $N_2^+ + H_2^+$ | 150 eV |

| Setting changed among samples | |
|---|---|
| Deposition and doping temperature | 400, 500 [°C] |
| Doping time | 0, 10, 30, 60 [min] |

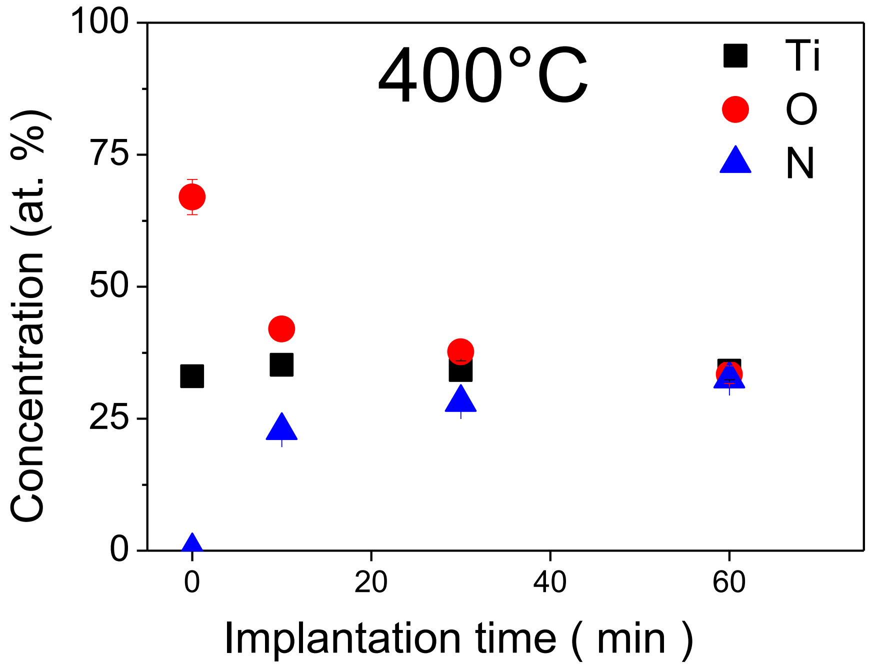
Vacuum base pressure: 0,2 mPa

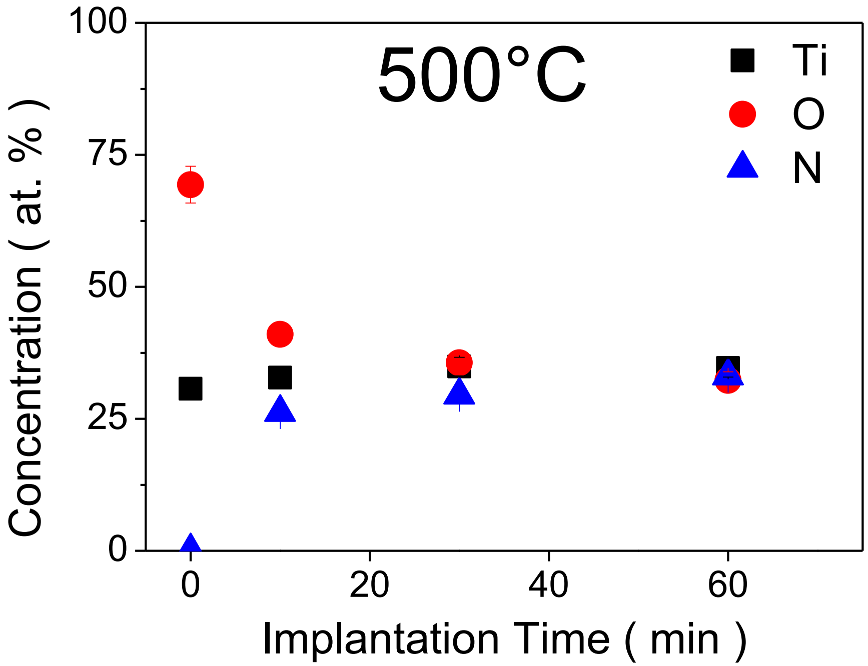
Leading to film thickness of about 85 nm.

Deposited on amorphous quartz substrate.

# Surface Composition

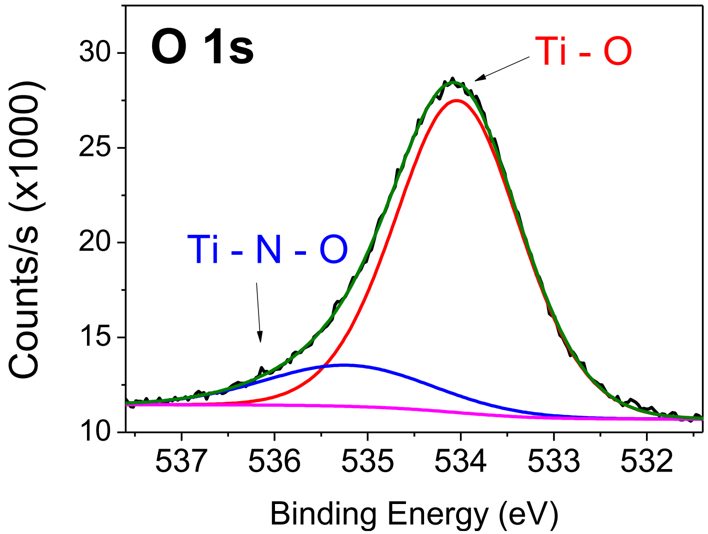
Determined by *in situ* XPS.

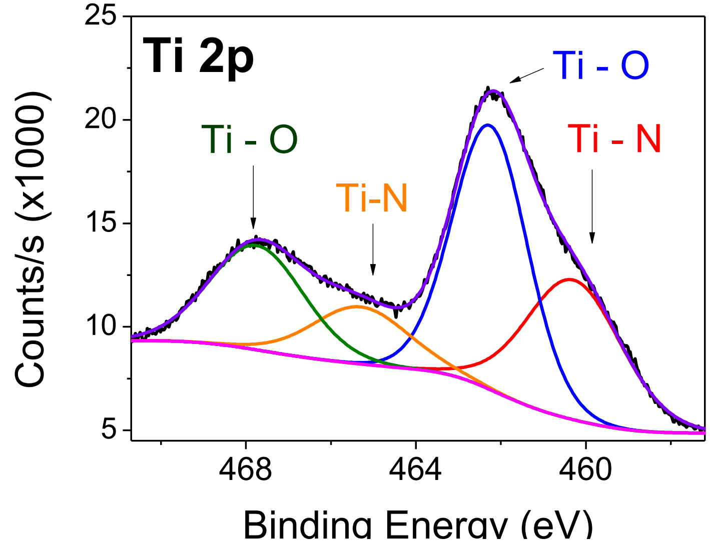


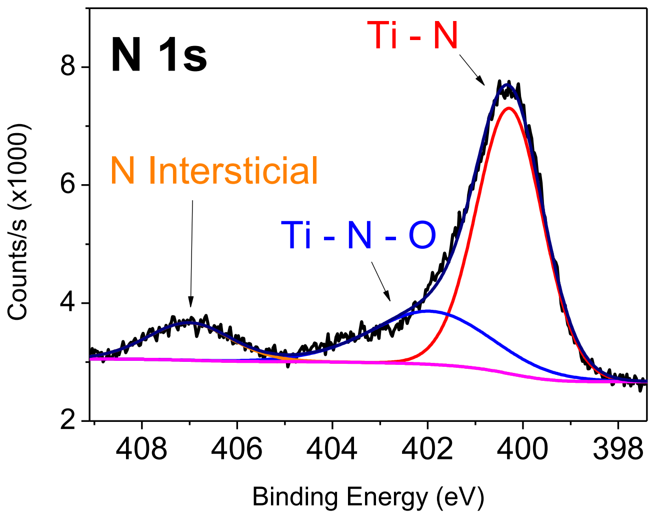




For both growth and doping temperatures,
**nitrogen** concentration increase in the surface up to about 30 at. % while **oxygen** concentration decreases.

# Chemical States



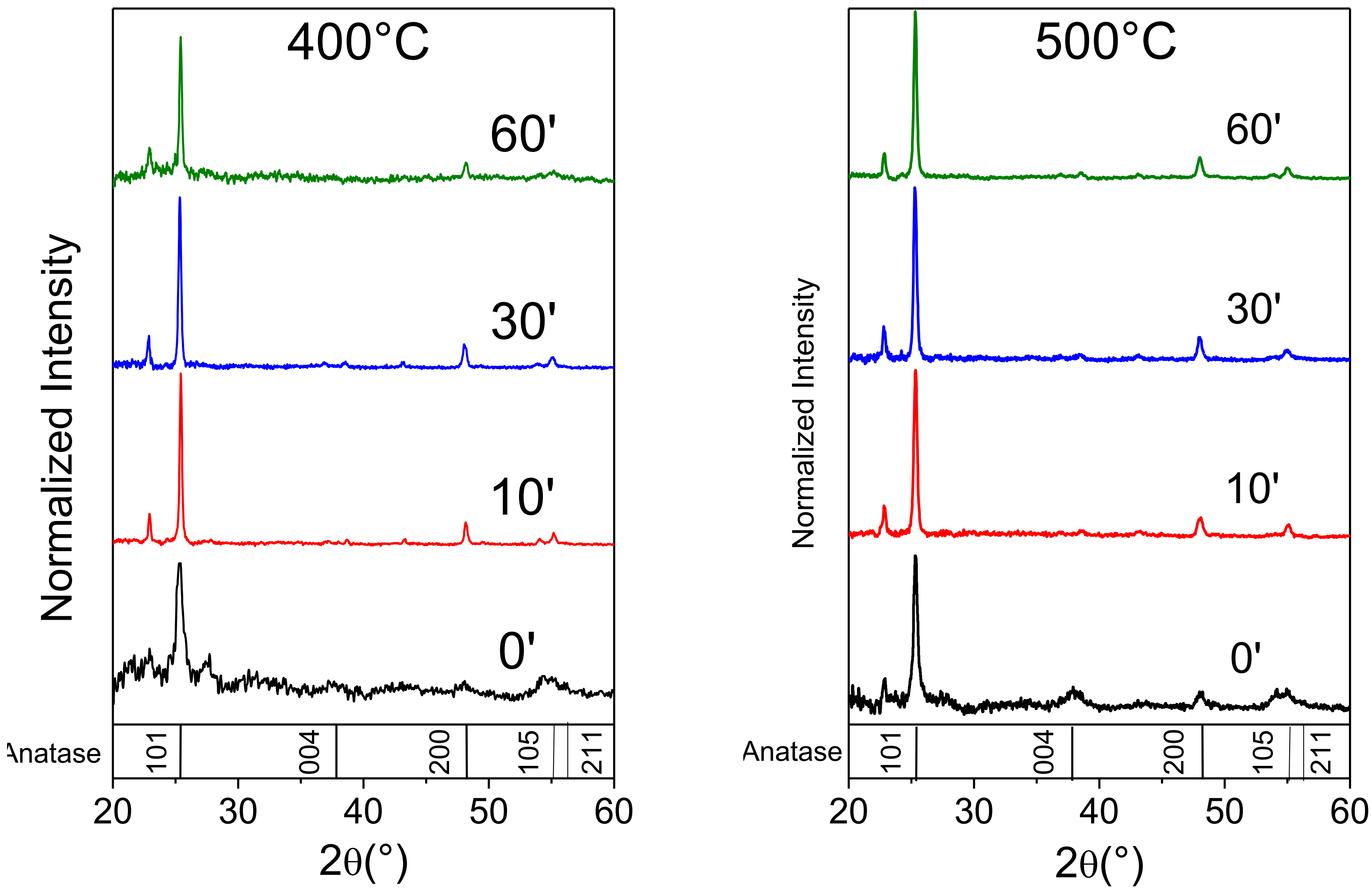




*In situ* XPS confirms the formation of chemical bonding among Ti, O and N.

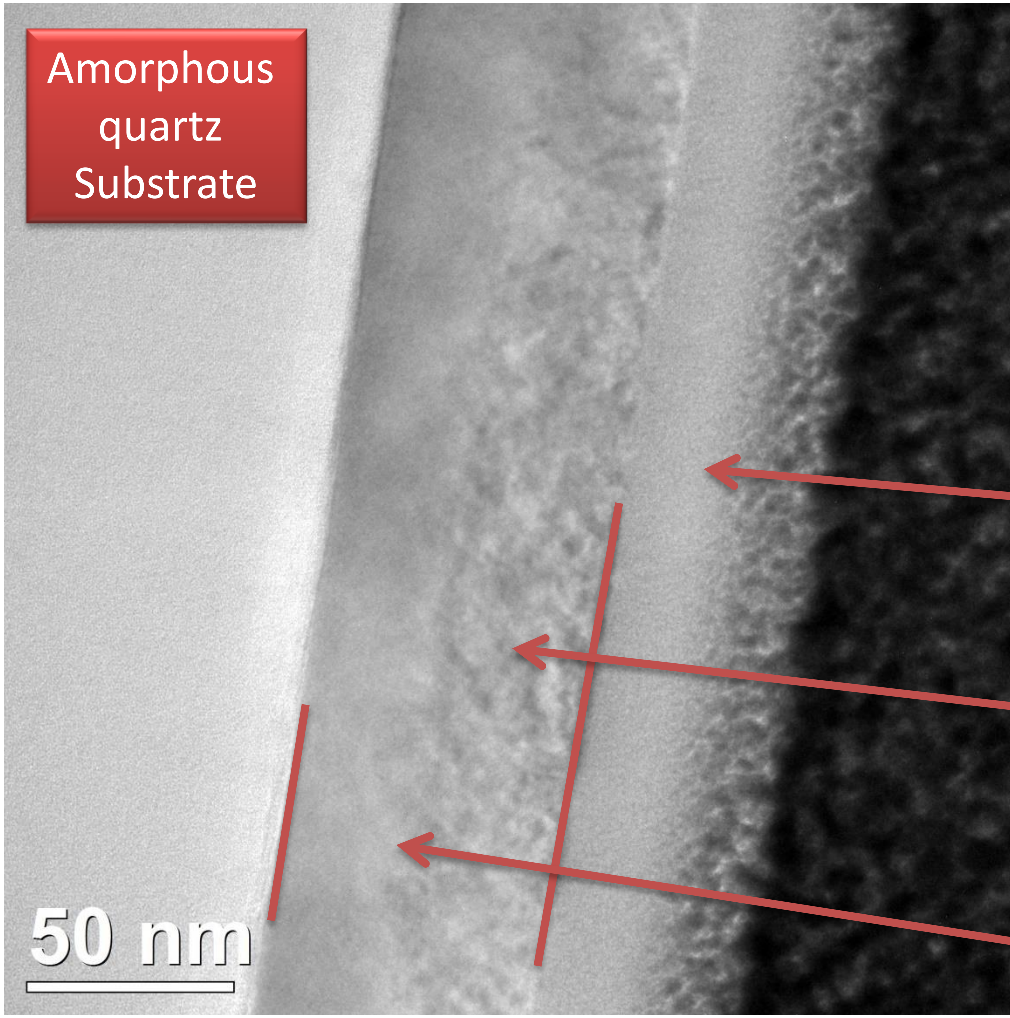
Ti 2p has TiN-like components, but the surface is not pure TiN.

# Crystal structure




Grazing incidence X-ray Diffraction confirms the formation of Anatase that indicates that this phase is preserved after doping (ion implantation).

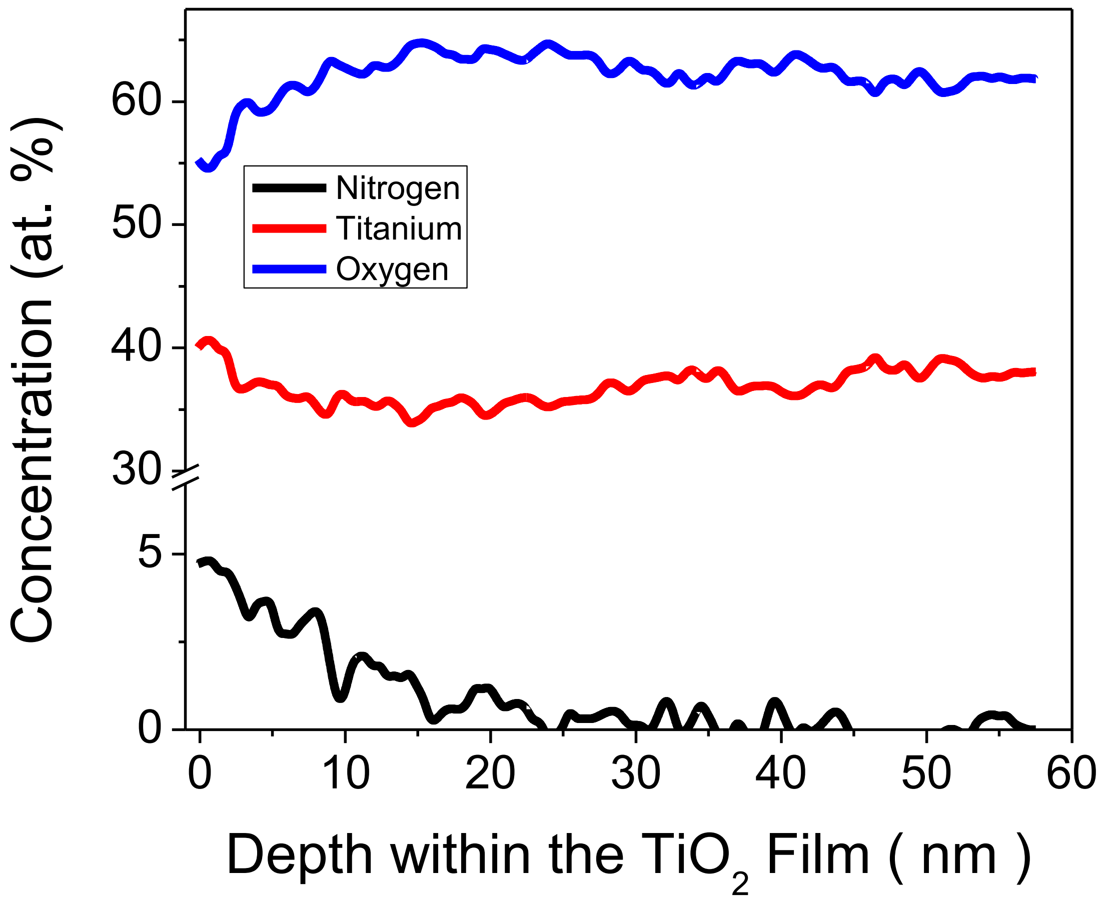
# Thin film morphology

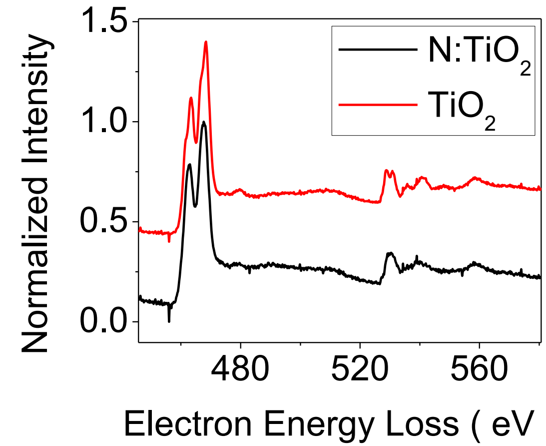


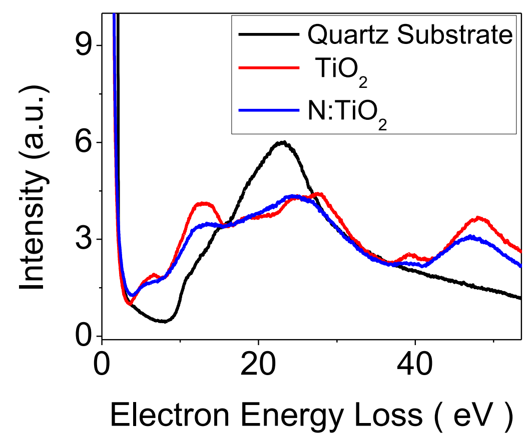

N:$TiO_2$ TEM cross-section.

Sample:
500°C – 60 minutes.

# Depth profiles



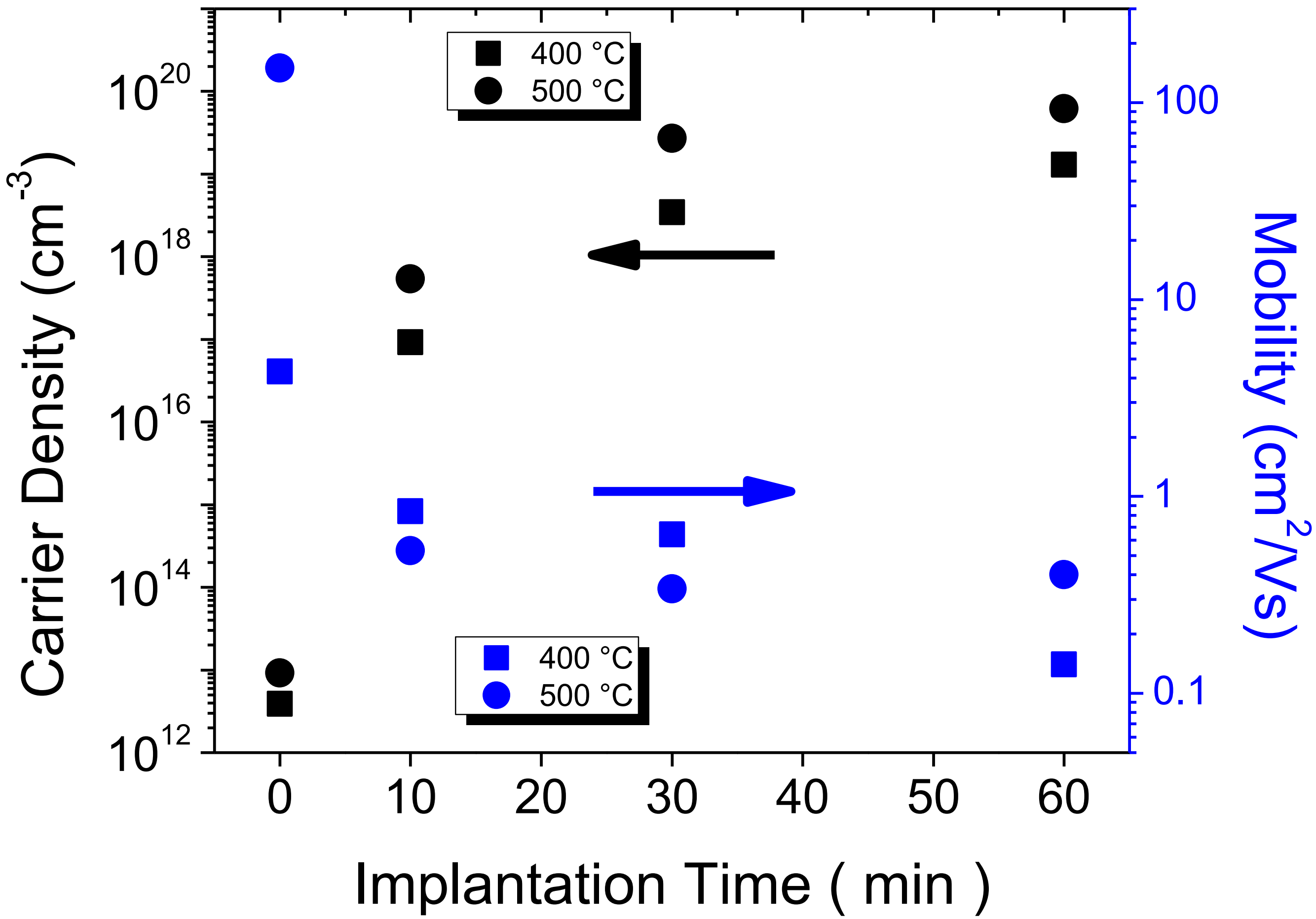




Electron Energy Loss (EELS) profiles indicate that Nitrogen diffuses at least up to ~20 nm. The dielectric function and Ti and O edges indicate changes down to ~30 nm.

# Electrical properties I

Carrier density up to ~ 6 × $10^{19}$ $cm^{-3}$.
Mobility fell to ~ 0.5 $cm^2/Vs$ (for 500°C – 60’ sample).
(Typical ITO values are $10^{21}cm^{-3}$ and 20 $cm^2/Vs$).

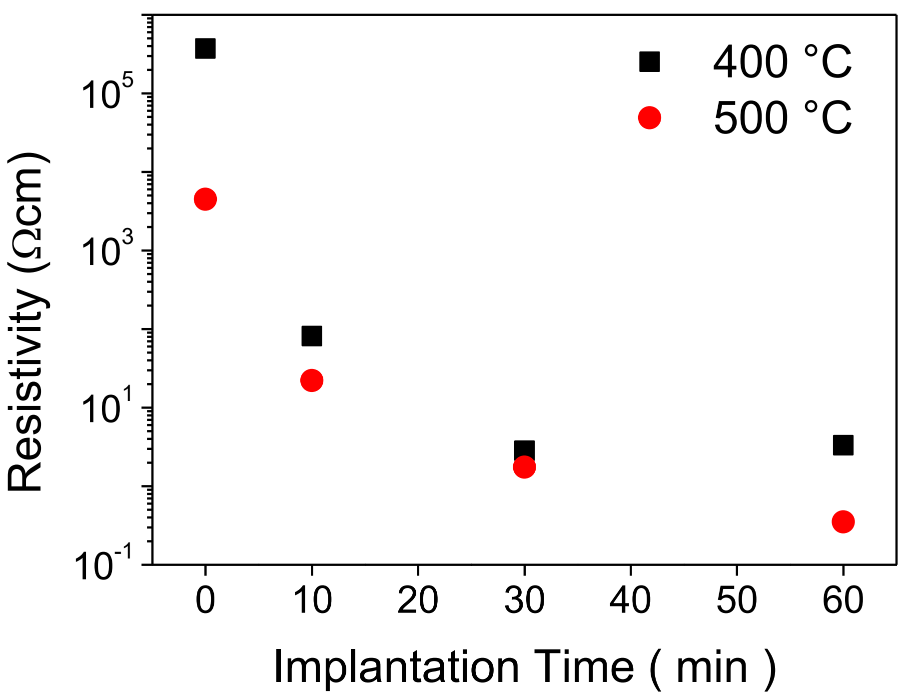



Hall Measurements with indium contacts.

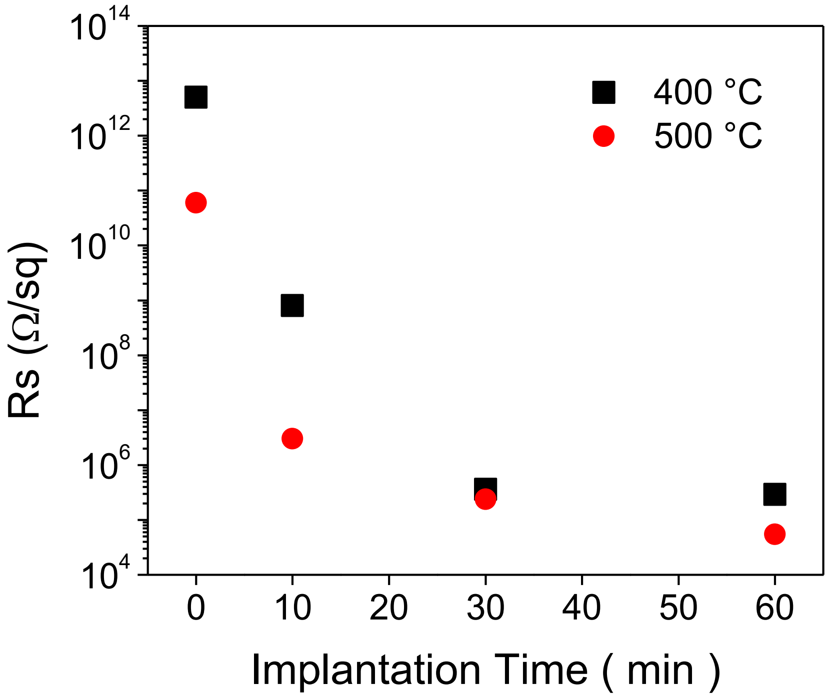
# Electrical properties II

Resistivity down to ~3 $10^{-1}$ Ωcm.
(ITO resistivity ~1 $10^{-4}$ Ωcm)
(for 500°C – 60' sample).

Agrees well with Hall resistivity.
Sheet resistance down to 55 kΩ.
(for 500°C – 60' sample).

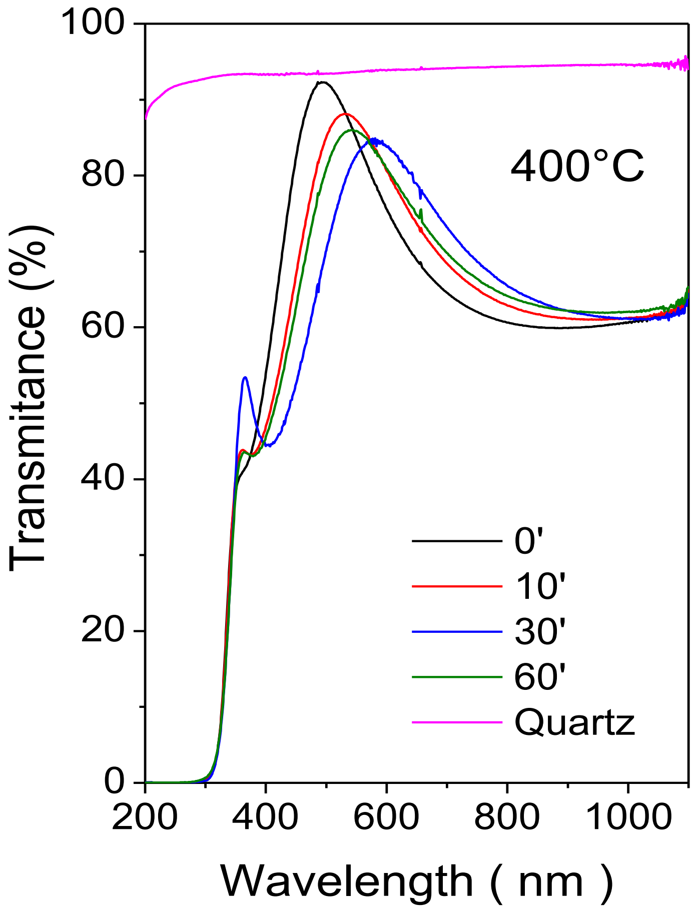


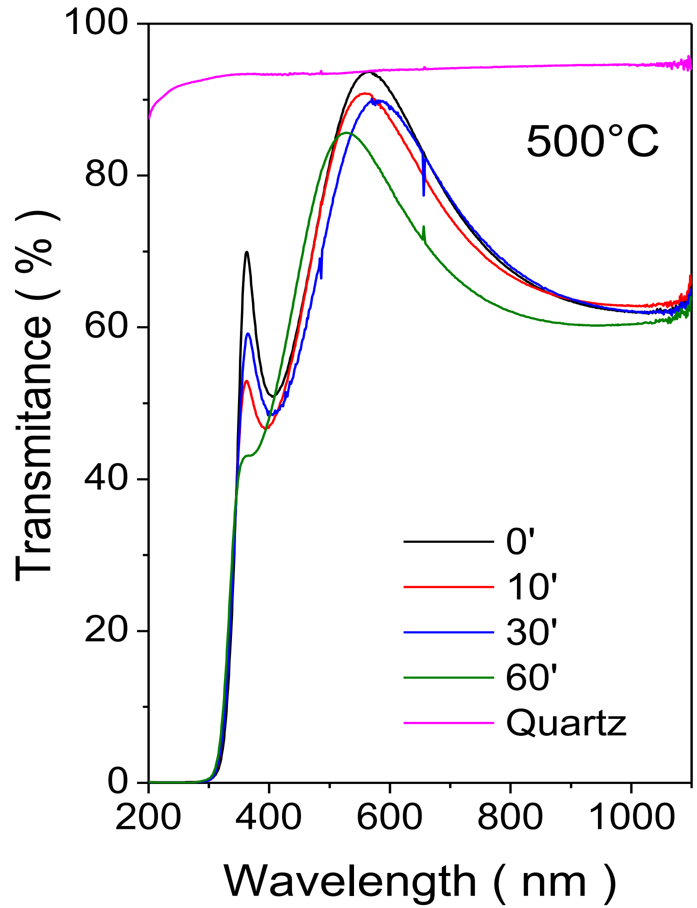

Hall Measurements
with indium contacts.




4-probe electrical
measurements

# Light transmission



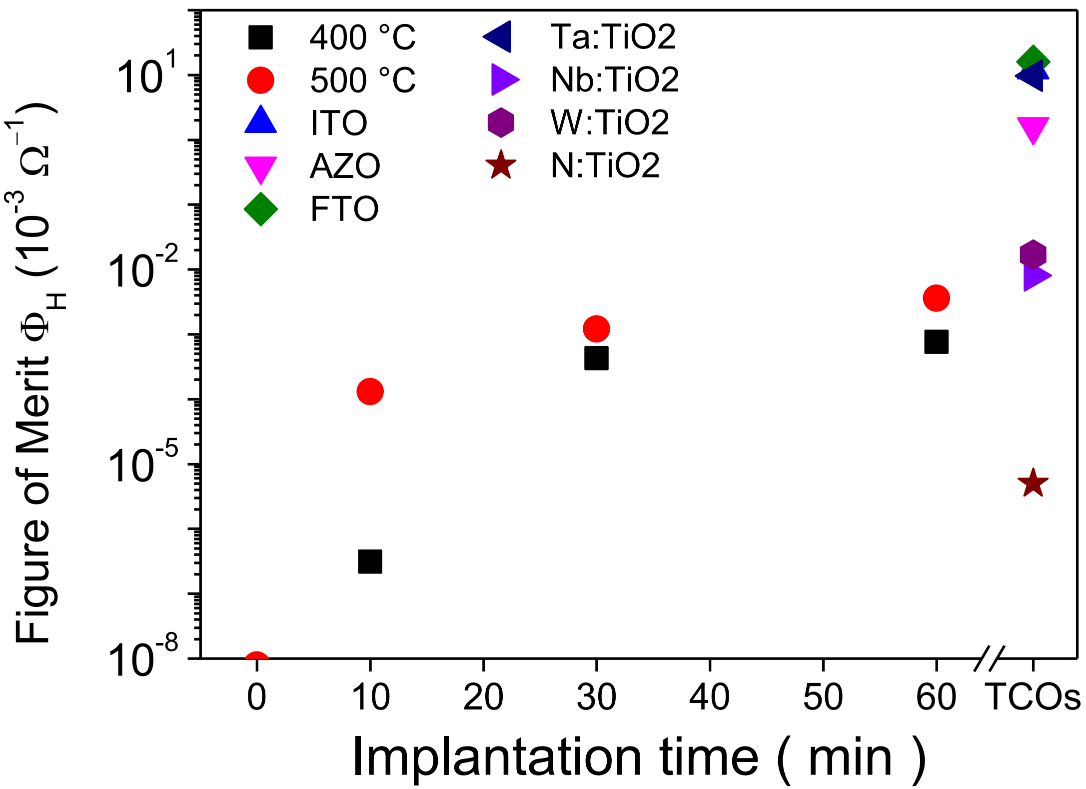

Bandgap: from 3.1 eV to 3.3 eV

Total transmission in the visible (measured by CCD spectrometer).

Transmittance between 80 and 90% at 550 nm.

Interference fringes are observed.

# Figure of Merit

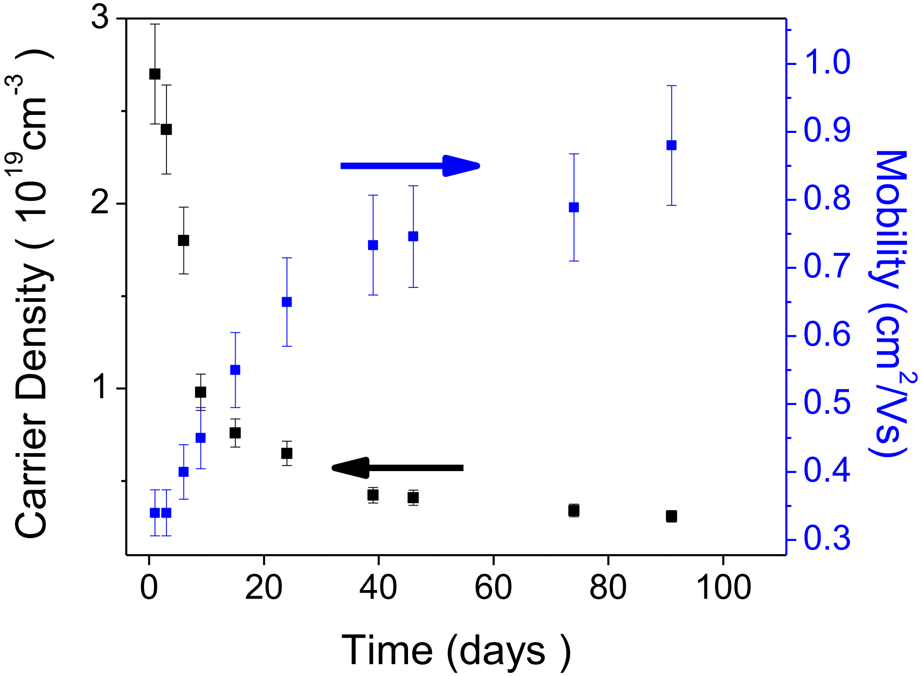


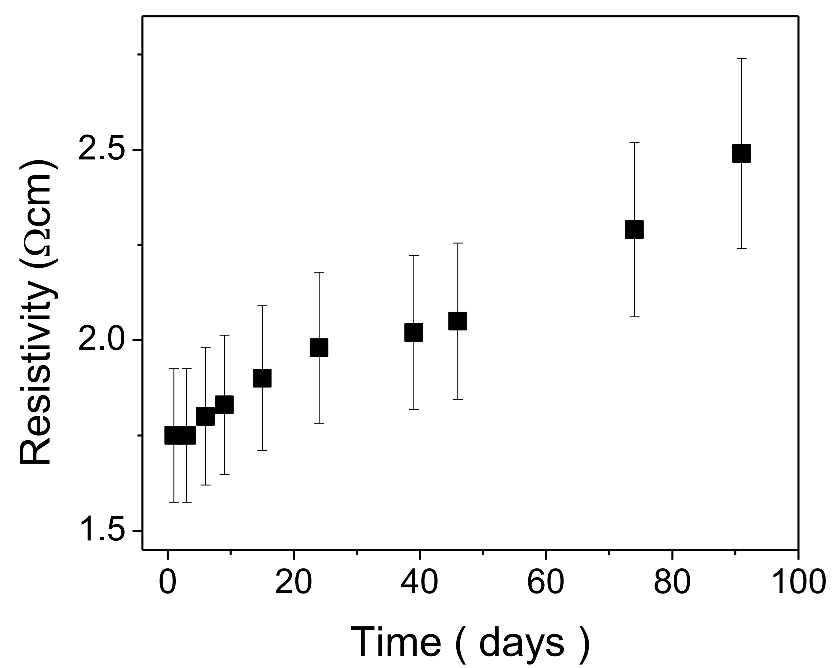

$$\Phi_H = \frac{T^{10}}{R_s} = e^{-10\alpha d}\sigma d$$

Figure of Merit is similar to some good literature results.

# Stability

Shelf stability for the 500°C – 30 minutes sample.




Low but significant changes in Mobility, Carrier density and Resistivity are observed.
Resistivity increased by ~40%.
Sample was **not** covered or protected by any passivation layer.

# Concluding remarks

- Low energy (400eV) ion implantation with $N^+$ ions is effective for $TiO_2$ doping.
- Nitrogen diffusion reached ~30 nm (1/3 of the $TiO_2$ film).
- Anatase phase is not significantly affected by doping up to ~6 $10^{19}$ $cm^{-3}$.
- Resistivity as low as ~3 $10^{-1}$ $\Omega$cm was obtained.
- We can speculate that longer nitriding times could lead to deeper diffusion, higher doping and lower resistivity.

# Acknowledgments

CNPq

CAPES

FAPESP

Thank you for kind your attention.