Optimization of the anti-reflective coating (SiCxNyH) / Silicon interface by the nitridation process to improve silicon photovoltaic cell performance

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Thin dielectric films are nowadays widely used for photovoltaic (PV) devices, for which both passivation of surfaces and anti-reflective properties are sought. Silicon wafer solar cells continue to be the leading photovoltaic technology. However, the interface between the Si substrate and its antireflective films play a key role in the yield of PV cells. A N_2 nitridation plasma process is developed to limit dangling bond formation and therefore to reduce the interface state density.

Nitridation process

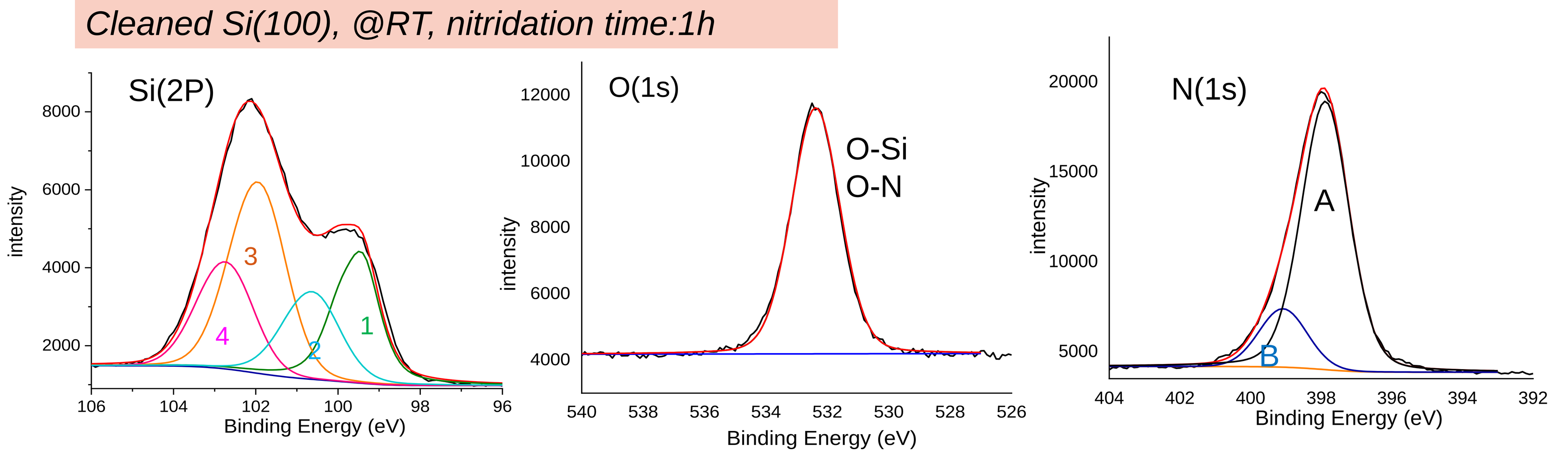
The Si(100) surfaces, as-received and cleaned are nitrided by N_2 GDS plasma sources and monitored by Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS) with take-off angle from 0° to 60°).
Experimental parameters : Nitridation temperatures (RT and 500° C) and time (1h-6h) were used to obtain the thin created nitride film.

Glow Discharge Source (GDS) parameters:
Majority of N^+ species
Power : 5 W / I_{sample}= 2 mA
P_{N2} : 10^{-4} mbar

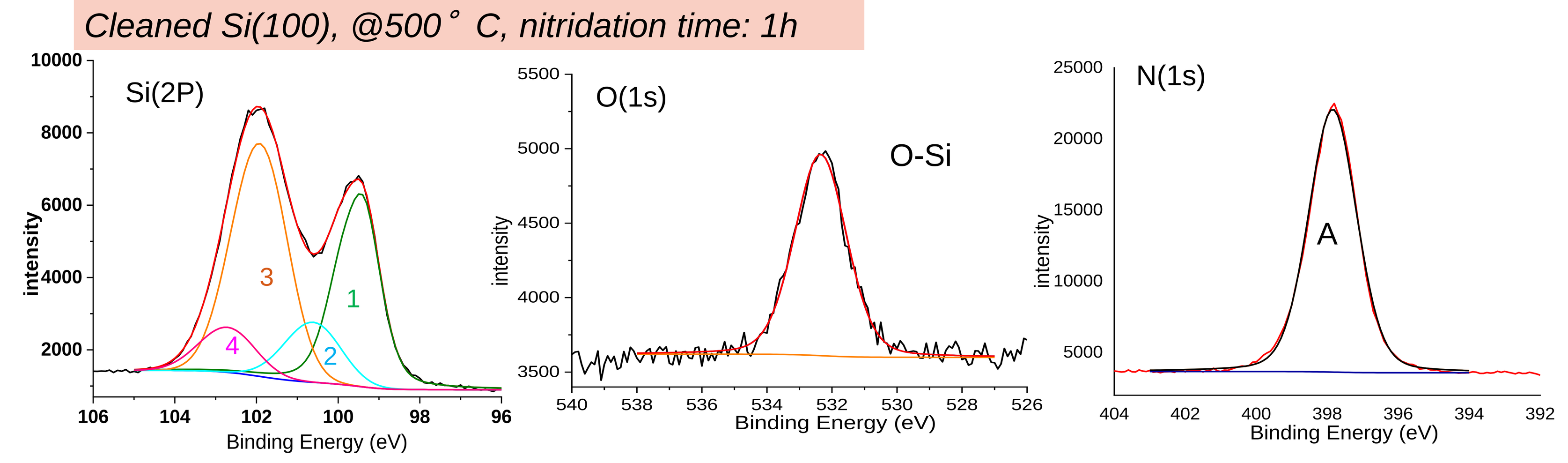
1. Effect of nitridation temperature : RT and 500° C

Peak	Si(2P)				O(1s)	N(1s)	
	Peak 1	Peak 2	Peak 3	Peak 4		Peak A	Peak B
Chemical bond	Si-Si	SiN_y (Y < 4/3) and SiO_x	Si_3N_4 and SiO_xN_y (X+Y≤3)	SiO_xN_y with dangling bonds ?	O-Si O-N	N-Si(ON_2) N-Si(O_2N)	N-O
Binding Energy (eV) FWHM	99.6[1] 1	100.8, [1] 1.45	102 [1] 1.45	102.8 1.45	532.6 [2] [1.8-2]	398.11[3] 1.6	399.45 1.6

Cleaned Si(100), @RT, nitridation time:1h



Cleaned Si(100), @500° C, nitridation time: 1h



- Presence of residual oxygen in the thin nitride layer
At 500° C nitridation temperature:
- Disappearance of the N-O contribution (N(1s))
- Intensity decrease of O(1s) peak and peak 4 (Si2P)

Effect of nitridation temperature: reduction of silicon dioxide

2. Comparison between as-received and cleaned Si(100)

Evolution of as-received/ cleaned Si(100) , @500° C, nitridation time:1h

	Cleaned Si(100)	As-received Si(100)
Peak 1/Peak 3	1.4	1.2
Peak 1/Peak 2	0.4	0. 38
Peak 1/Peak 4	0.33	0. 37
Peak 1/N1s	0.21	0.24
Peak 1/O1s	2.5	1.81
N/O	11.90	7.54

Little influence of the initial state of the Si substrate @ 500° C nitridation temperature

Nitrogen diffusion in Si matrix and creation of thin nitride layer (SiON) (<9 nm) with residual oxygen reduced by nitridation temperature (500°C) tending to create Si dangling bonds

Outlooks

- ❑ What is the contribution of this ultra thin nitride layer ?
- ❑ Electrical measurements coupled with physico-chemical study will be considered in order to evaluate the interfacial state density and improve the silicon photovoltaic cell performance.

References :
[1] Journal of Applied Physics 97 (2005) 073518
[2] Thermo Scientific X-ray Photoelectron Spectroscopy XPS
[3] Surface and Coatings Technology 174 –175 (2003) 370–374

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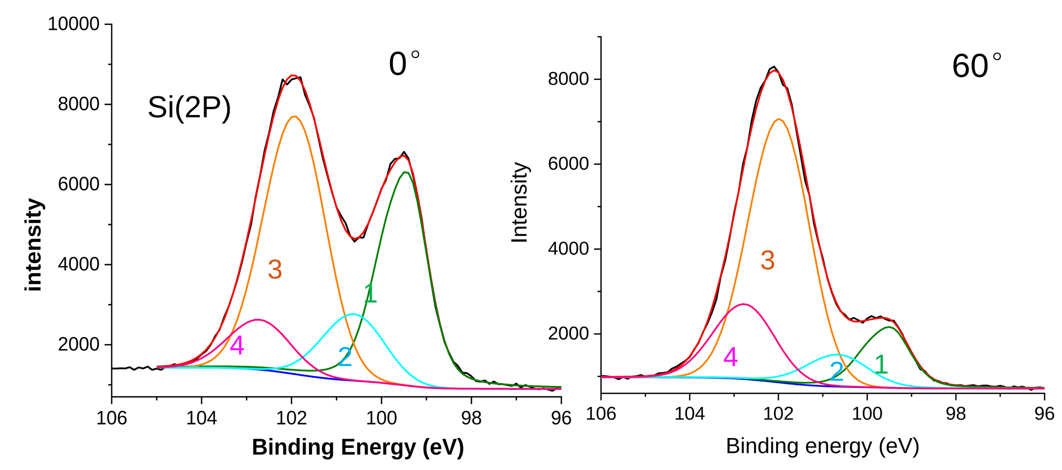
3. Study by AR-XPS of the thin nitride film

Cleaned Si(100) , @500° C, nitridation time [1h-6h], take off angle [0° -60°] AR-XPS



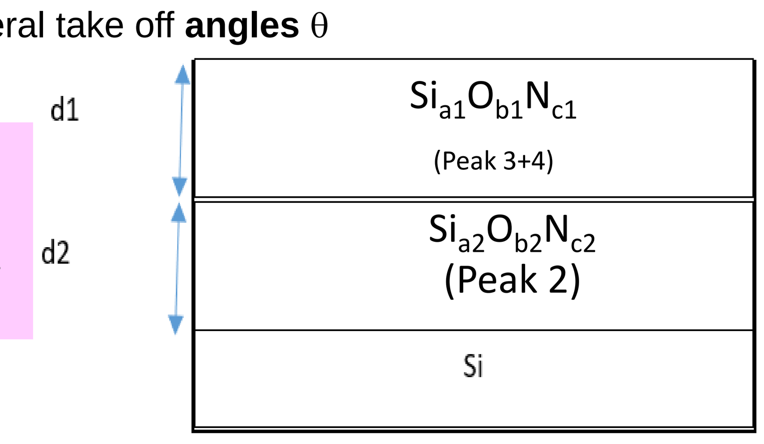
Case of Si(2P) peak :
I(Peak 2) / I(Si(2p)) =
I(Peak 3) / I(Si(2p)) ↗
I(Peak 4) / I(Si (2p)) ↗

AR-XPS : building of a layered model

Fine modeling of AR-XPS signals: MATLAB programming

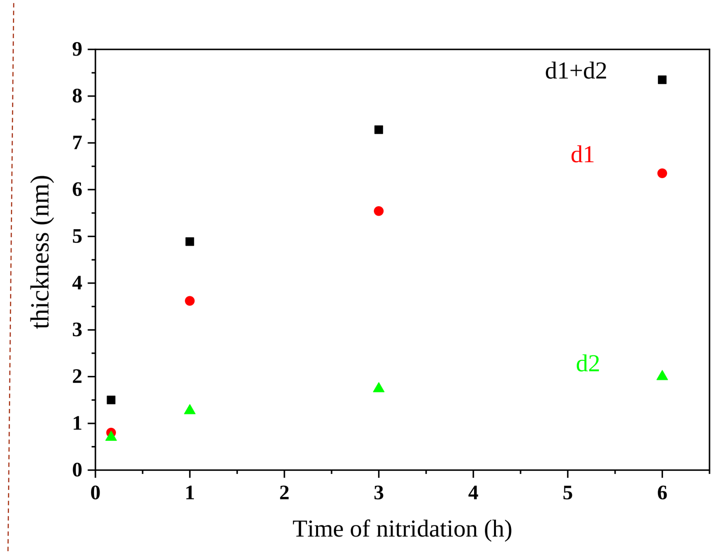
Comparison between theoretical and experimental intensity for several take off **angles** θ

Constraints :
a1 < a2 Si-rich interfacial layer
a2 ≤ 0,66 Layer 2 corresponds to the contribution of peak 2
(Si_2O: a2=2/3 =0,66 and/or Si_3N_2: a2=3/5 = 0,6 [1])



Determination of the stoichiometry (a, b, c) and thickness (d) of the two $Si_aO_bN_c$ layers

4. Effect of nitridation time

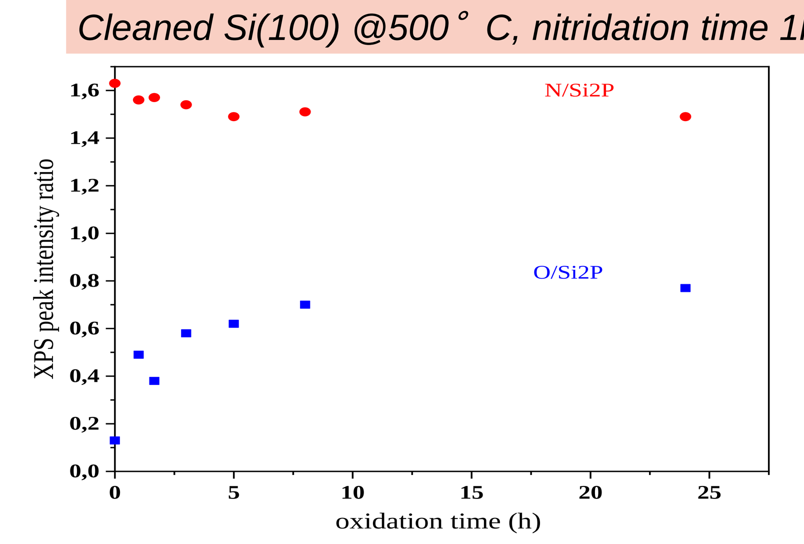


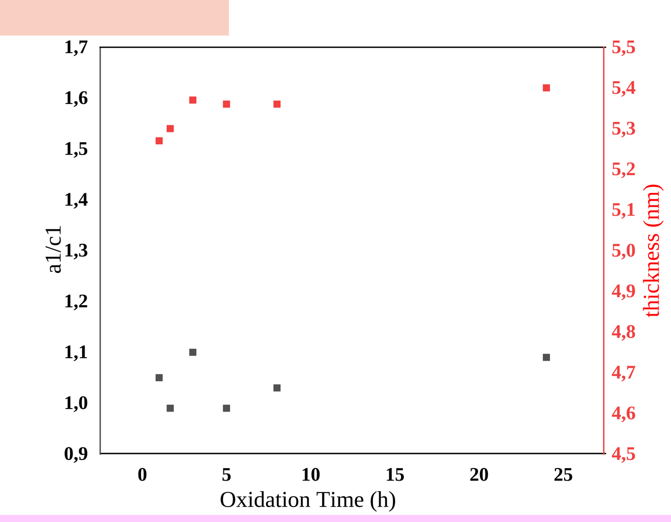
- No stochiometry changes versus nitridation time [1h-6h]
  0.45<a1<0.50, b1=0, 0.45<c1<0.50
  0.50<a2<0.60, 0.30<b2<0.50, c2<0.10
- Nitridation process saturation after 6h : Nitride layer thickness less than 9 nm
- Layer 2 : very thin interfacial layer (<2 nm)
- Layer 1 : d1 increases faster than d2

Effect of a post oxidation

This aims to study the chemical behavior of the nitrided layer between the two processes : the silicon nitridation and the anti-reflective coating growth

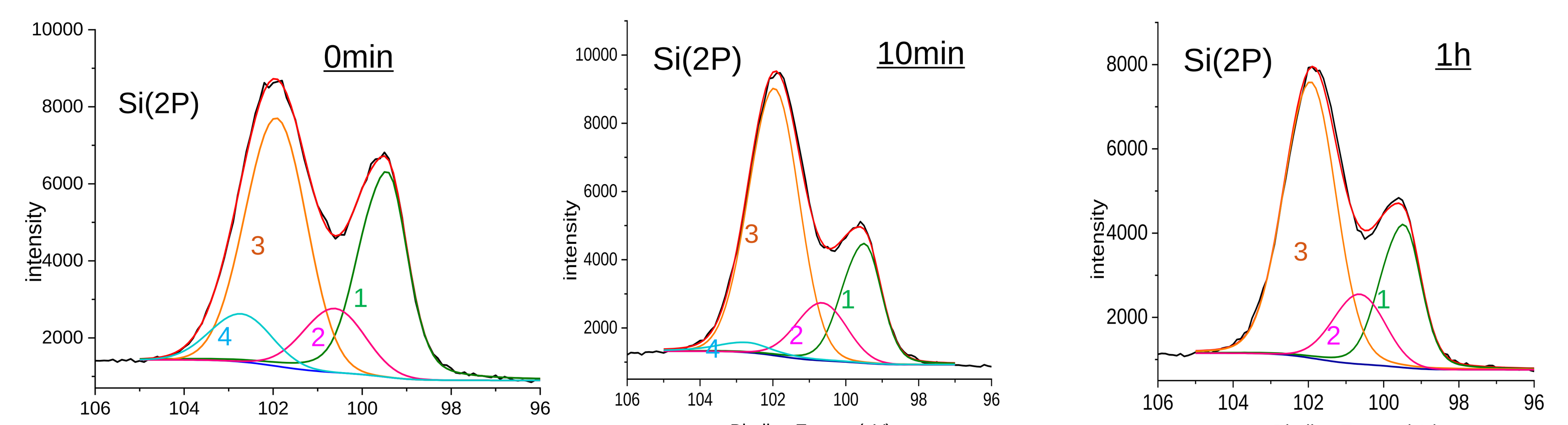
Cleaned Si(100) @500° C, nitridation time 1h





- Increase of oxygen during the first hour of air exposure
- The Nitrogen amount is constant

- **a_1/c_1=[Si]/[N]=cste→** No substitution of nitrogen by oxygen: No destruction of Si-N bonds
- b_1 in the range of [0.05-0.1]= surface
- Little increase of the nitride layer with air exposure (oxydation)



- Extinction of peak 4 between 10 mn and 1h of air exposition : oxydation of dangling bonds

Peak 4 corresponding to SiON with dangling bonds

Air exposure leads to the passivation of the defects (filling Si dangling bonds)