Swelling and optical properties of Si_3N_4 films irradiated in the electronic regime

B. Canut [a],*, A. Ayari [b], J. Dupuis [a], M. Lemiti [a], A. Fave [a], S. Ramos[c]

[a] Institut des Nanotechnologies de Lyon, Université de Lyon, Université Claude Bernard Lyon 1 ;
CNRS, UMR 5270 ; Domaine Scientifique de la Doua ; F-69622 Villeurbanne, France

[b] Centre de Recherche en Nanofabrication et Nanocaractérisation, Université de Sherbrooke, Canada

[c] Laboratoire de Physique de la Matière Condensée et Nanostructures, Université de Lyon, Université
Claude Bernard Lyon 1 ; CNRS, UMR 5586 ; Domaine Scientifique de la Doua ; F-69622
Villeurbanne, France

Abstract

Silicon nitride layers of 140 nm thickness were deposited on silicon wafers by low pressure chemical vapour deposition (LPCVD) and irradiated at GANIL with Pb ions of 110 MeV up to a maximum fluence of 4 x 10^{13} cm^{-2}. As shown in a previous work these irradiation conditions, characterized by a predominant electronic slowing-down (S_e = 19.3 $keV.nm^{-1}$), lead to damage creation and formation of etchable tracks in Si_3N_4. In the present study we investigated other radiation-induced effects like out of plane swelling and refractive index decrease. From profilometry, step heights as large as 50 nm were measured for samples irradiated at the highest fluences (> 10^{13} cm^{-2}). From optical spectroscopy, the minimum reflectivity of the target is shifted towards the high wavelengths at increasing fluences. These results evidence a concomitant decrease of density and refractive index in irradiated Si_3N_4. Additional measurements, performed by ellipsometry, are in full agreement with this interpretation.

PACS : 61.82.Ms ; 61.72.Ff ; 68.37.Ps

Key words : Irradiation, silicon nitride, swelling, optical properties.

* Corresponding author.

Tel. : +33 4 72 43 87 34 ; Fax : +33 4 72 43 85 31

E-mail address : bruno.canut@insa-lyon.fr

1. Introduction

Due to its favourable mechanical, chemical and optical properties, silicon nitride finds many applications in microelectronics. For instance, this material can serve as a gate dielectric in field effect transistors [1], as a charge storage layer in non-volatile memories [2], as a barrier for moisture or dopant diffusion [3] or as an antireflection coating for photovoltaic cells [4]. Among the numerous techniques which allow the deposition of silicon nitride films, we have chosen low-pressure chemical-vapour-deposition (LPCVD) which presents the advantage of processing stoichiometric and homogeneous Si_3N_4 layers with a high refractive index [5]. Despite its fundamental interest and the potential applications involved, the response of silicon nitride to swift heavy ion irradiation remains still little studied, except in the case of a single crystalline target [6]. In a previous work [7], we have evidenced damage creation and formation of etchable tracks in amorphous Si_3N_4 layers deposited on silicon by LPCVD. The aim of the present study was to complement these investigations by studying other radiation-induced effects like out of plane swelling and refractive index lowering.

2. Experimental procedure

The starting substrates were Cz-grown N type Si(100) wafers with a resistivity of ≈ 1 Ω.cm. Silicon nitride films were prepared in an industrial type LPCVD reactor by using the reaction of diluted silane (SiH_4/Ar = 10%) with amonia (NH_3) at a temperature of 800°C [8]. According to profilometry measurements and Rutherford backscattering spectrometry (RBS), the film thickness and its density were 140 nm and 3.1 $g.cm^{-3}$, respectively. The samples were irradiated with Pb ions of 110 MeV accelerated at the IRRSUD beamline of GANIL accelerator in Caen (France). According to SRIM2006 code [9], the electronic and nuclear stopping powers at the nitride surface were $S_e = 19.3$ $keV.nm^{-1}$ and $S_n = 0.35$ $keV.nm^{-1}$, respectively. The fluences ranged from 10^9 to 4×10^{13} cm^{-2} on a 5×5 cm^2 irradiated surface and the irradiation flux was limited to 10^9 $cm^{-2}.s^{-1}$ in order to avoid any overheating of the targets. The radiation-induced disorder was investigated by Fourier transform infrared spectroscopy (FTIR) using a “Spectrum 2000” Perkin Elmer spectrophotometer operating in the 370 cm^{-1} – 7800 cm^{-1} wavenumber range. Swelling effects were evidenced from step height measurements between the irradiated zone and a pristine area, using a Tencor “Alphastep” profilometer. In order to study the influence of ion bombardment on the refractive index of Si_3N_4, we have combined profilometry (determination of the film thickness after irradiation) with optical reflectivity measurements in the 200 – 2500 nm wavelength range. This latter technique was performed using a “Lambda 900” Perkin Elmer spectrophotometer. The optical characterizations were complemented by ellipsometric measurements using a Jobin Yvon “UVISEL” spectroscopic ellipsometer.

3. Results and discussion

3.1 Radiation-induced disorder and swelling

The infrared absorption bands ascribed to Si-N bondings occupy the 740 – 1050 cm^{-1} wavenumber range [10]. After baseline substraction from the raw FTIR spectra, they are plotted in figure 1 before and after irradiation. The decrease of absorbance versus the fluence Φ indicates a destruction of nitrogen bonds as a result of ion bombardment. The radiation-induced disorder in Si_3N_4 was determined from the relative amount Q of remaining Si-N bonds at a given fluence. This parameter was defined as $Q = \frac{I}{I_0}$, where I_0 and I are the area of the absorption band corresponding to the virgin and irradiated target, respectively. Figure 2a shows the evolution of Q versus the fluence Φ. This kinetics exhibits a rapid decrease of Q at low fluences ($\approx 10^{12}$ cm^{-2}) followed by a slope change at intermediate fluences ($\approx 5 \times 10^{12}$ cm^{-2}) and by a further decrease at slow rate at the highest fluences. A sputtering process superimposed to the disorder creation could account for such a fluence dependence. However, this hypothesis must be ruled out as complementary characterizations, using Rutherford backscattering spectrometry (RBS), did not evidence any significant material losses after irradiation. Following a description given in a previous paper [7], the kinetics displayed in figure 2a was interpretated assuming that the disorder creation in silicon nitride occurs via both electronic and nuclear processes. By denoting σ_e and σ_n the respective cross-sections associated to these two mechanisms, we have fitted the experimental data by two-exponential decay functions :

$$Q = Q_s.\exp(-\sigma_n.\Phi) + (1 - Q_s).\exp(-\sigma_e.\Phi) \qquad (1)$$

A good agreement of the data was obtained by using the following fit parameters : $Q_s = 71$ %, $\sigma_e = 76$ nm^2 and $\sigma_n = 0.7$ nm^2. This latter value is by one order of magnitude higher than the nuclear damage cross-section as calculated by the help of the SRIM code assuming a conventional displacement energy $E_d = 30$ eV for the target atoms. A synergy between the damage processes via elastic and inelastic slowing-down could possibly explain this discrepancy. In other words, the breaking of Si-N bonds by electronic excitations probably lowers the displacement threshold energies of Si and N atoms. Another striking consequence of the irradiation is the target swelling. Step height measurements, deduced from profilometer scans across the border between the pristine and the bombarded zones are reported as a function of the fluence in figure 2b. The obtained kinetics seems to follow a S-shaped curve, suggesting a two (or more) step process for the target swelling. However, the limited number of data (especially at low fluences) and the experimental uncertainties hinder us to confirm this hypothesis. For this reason, we have simply fitted the fluence evolution of ΔX by using a Poisson law given by :

$$\Delta X = \Delta X_s . (1 - \exp(-\sigma_s \Phi)) \qquad (2)$$

The saturation value, $\Delta X_s = 51$ nm, is very high since it exceeds one third of the initial layer thickness (e = 140 nm). Due to the high fluences used, the nuclear damage created in the underlying silicon substrate could play a role in the volume expansion of the irradiated target. However, profilometer scans performed on irradiated samples after further complete etching of the nitride layer (using 10 %

vol. HF during one hour) did not evidence any more step height. As a consequence, the swelling occurs only in the Si_3N_4 layer. Many previous works have been devoted to the swelling of insulators irradiated in the electronic regime. In these studies, performed using single crystalline targets, the density loss responsible for the volume expansion was explained by a crystalline-amorphous phase change in the case of covalent materials [11, 12] or by a transition to a nanocrystalline structure or defect aggregates in the case of non-amorphizable ionic materials [13, 14]. In the present case, the silicon nitride layer is already amorphous and the very high step height values measured after irradiation could originate from the relaxation of the stress generated in the film during the LPCVD process. Profilometry performed with scans larger than those used in the present work would allow to measure the bending of the entire sample and thus to confirm this hypothesis. Moreover, the fitting according equation (2) leads to a swelling cross-section $\sigma_s = 9.4 \times 10^{-14}$ cm^2 which is eight times lower than the damage cross-section σ_e via electronic processes. This result shows that only a small part of the radiation-induced track contributes to the out of plane expansion of the silicon nitride target.

3.2 Refractive index change

Figure 3 displays the reflectivity spectra recorded on Si_3N_4/Si targets before and after irradiation at different fluences. In all cases, an antireflective behaviour is evidenced. The reflectivity R is close to zero at a characteristic wavelength $\lambda^* = 4nt$, where n is the refractive index of the nitride layer and t its thickness. At increasing irradiation fluences, one can note a shift of the spectra towards the high wavelenghts, indicating an increase of the product $n(\Phi).t(\Phi)$. From the profilometry measurements described above, we obtain a film thickness : $t = e + \Delta X$. As a consequence, the determination of λ^* from reflectivity allows the determination of n according to the following relation :

$$n = \frac{\lambda^*}{4\,(e + \Delta X)} \qquad (3)$$

In this approach, we neglegt the small wavelength dependence of n over the range covered by the λ^* values (1100 nm- 1300 nm). The evolution of n as a function of the fluence Φ is plotted in figure 4a. Before irradiation ($\Phi = 0$), one obtains n = 1.97 which is close to the reported value of 2.0 for stoichiometric Si_3N_4 films [15]. After irradiation, the refractive index falls down to a minimum value of 1.71 for the maximum fluence (4×10^{13} cm^{-2}). This trend, confirmed by ellipsometry, can be ascribed to the swelling effect which implies a decrease of the target density. According to the well-known Clausius-Mosotti formula, the refractive index of a dielectric material obeys the following expression :

$$\frac{n^2-1}{n^2+2} = \frac{N_A.\alpha}{3M} \bullet \rho \qquad (4)$$

, where N_A is the Avogadro number, α is the atomic polarisability, M is the molecular mass and ρ is the material density. Assuming that the layer expansion occurs only along the beam direction (X), the relative volume change of the layer is given by $\frac{\Delta V}{V} = \frac{\Delta X}{e}$. Consequently, the density ρ of the irradiated layer can be deduced from step height data as : $\rho = \rho_0 \bullet \frac{e}{e+\Delta X}$, where ρ_0 is the density of a pristine LPCVD Si_3N_4 film ($\rho_0 = 3.1$ $g.cm^{-3}$). By denoting x the relative density $\frac{\rho}{\rho_0} = \frac{e}{e+\Delta X}$ and y the ratio $\frac{n^2-1}{n^2+2}$, the equation (4) may be rewritten as :

$$y = \frac{N_A.\alpha.\rho_0}{3M} \bullet x \qquad (5)$$

These parameters x and y are not independent, as they are both function of the irradiation fluence. However, according to equation (5), the couples (x, y) calculated at each fluence from the results displayed in figures 2b and 4a should align along a straight line passing through the origin. The data displayed in figure 4b are in full agreement with this criterion, except in the cases of the two highest fluences (2×10^{13} and 4×10^{13} cm^{-2}). In addition to the possible experimental uncertainties, one can invoke a variation of the atomic polarisability α at high damage levels to explain these deviations from a pure linear fitting.

4. Conclusion

In this work, we have shown that swift heavy ions in the electronic regime induce damage in LPCVD Si_3N_4 layers. The radiation-induced disorder is accompanied with very large out of plane swellings, leading to a decrease of the target density up to 35 % for the highest fluences. This effect was ascribed to the relaxation of the stress present in the as-processed samples. Complementary experiments, using Raman spectroscopy or bending measurements, are required to confirm this hypothesis. The fluence evolution of the Si_3N_4 refractive index, extracted from reflectivity and profilometry, was fitted satisfactory in the framework of the Clausius-Mosotti theory. In a future work, we plan to perform irradiations using different electronic stopping powers and projectile velocities, in order to precise the threshold for swelling and to study the influence of the damage morphology (continuous or discontinuous tracks) on the refractive index change.

References

[1] M. Moslehi, K.C. Saraswat, S.C. Shatas, Appl. Phys. Lett. 47 (1985) 1113.

[2] D. Frohman-Bentchkwsky, M. Lenzlinger, J. Appl. Phys. 40 (1969) 3307.

[3] E.P. EerNisse, J. Appl. Phys. 48 (1977) 3337.

[4] A.G. Aberle, Sol. Energy Mater. Sol. Cells 65 (2001) 239.

[5] G. Beshkov, V. Lazarova, D.B. Dimitrov, J. Non Cryst. Sol. 187 (1995) 301.

[6] S.J. Zinkle, V.A. Skuratov, D.T. Hoelzer, Nucl. Instr. and Meth. B 191 (2002) 758.

[7] B. Canut, A. Ayari, K. Kaja, A-L. Deman, M. Lemiti, A. Fave, A. Souifi, S. Ramos, Nucl. Instr. and Meth. B 266 (2008) 2819.

[8] B. Semmache, M. Lemiti, Ch. Channelière, Ch. Dubois, A. Sibai, B. Canut, A. Laugier, Thin Solid Films 296 (1997) 32.

[9] J.F. Ziegler, J.P. Biersack, U. Littmark, *Stopping Power and Ranges of Ions in Matter*, Vol. I, Pergamon, New York, 1985.

[10] M. Klanjsek Gunde, M. Macek, Phys. Stat. Sol. (a) 183, 2 (2001) 439.

[11] B. Canut, R. Brenier, A. Meftah, P. Moretti, S. Ould Salem, S. Ramos, P. Thevenard, M. Toulemonde, Nucl. Instr. and Meth. B 91 (1994) 194.

[12] M. Toulemonde, A; Meftah, J.M. Costantini, K. Schwartz, C. Trautmann, Nucl. Instr. and Meth. B 146 (1998) 426.

[13] C. Trautmann, M. Toulemonde, J.M. Costantini, J.J. Grob, K. Schwartz, Phys.Rev. B62 (2000) 13.

[14] C. Trautmann, M. Boccanfuso, A. Benyagoub, S. Klaumünzer, K. Schwartz, M. Toulemonde, Nucl. Instr. and Meth. B 191 (2002) 144.

[15] E. Paule, E. Elizalde, J.M. Martinez-Duart, J.M. Albella, Vacuum 37 (1987) 395.

Figure captions

Figure 1 : Evolution of the Si-N absorption band (after baseline substraction) as a function of the irradiation fluence (110 MeV Pb irradiations).

Figure 2 : Fluence dependences of disorder and swelling in irradiated Si_3N_4 .

(a) Relative amount of the Si-N bondings deduced from FTIR spectroscopy. The continuous curve is a fitting to the data using a double exponential decay function.

(b) Step height measurements deduced from profilometry. The continuous curve is a fitting to the data using a single exponential decay function.

Figure 3 : Reflectivity spectra of Si_3N_4 / Si targets before and after irradiation at increasing fluences.

Figure 4 : Influence of the irradiation on the refractive index n of LPCVD Si_3N_4

(a) Evolution of n (deduced from reflectivity and profilometry) versus the fluence Φ. The continuous curve is drawn to guide the eye.

(b) Ratio $y = \frac{n^2 - 1}{n^2 + 2}$ versus the relative density $x = \frac{\rho}{\rho_0}$ of irradiated Si_3N_4.
The dashed straight line passing through the origin fits most of data ($\Phi \leq 10^{13}$ cm^{-2}) via the Clausius-Mosotti formula (assuming a constant polarisability α) .

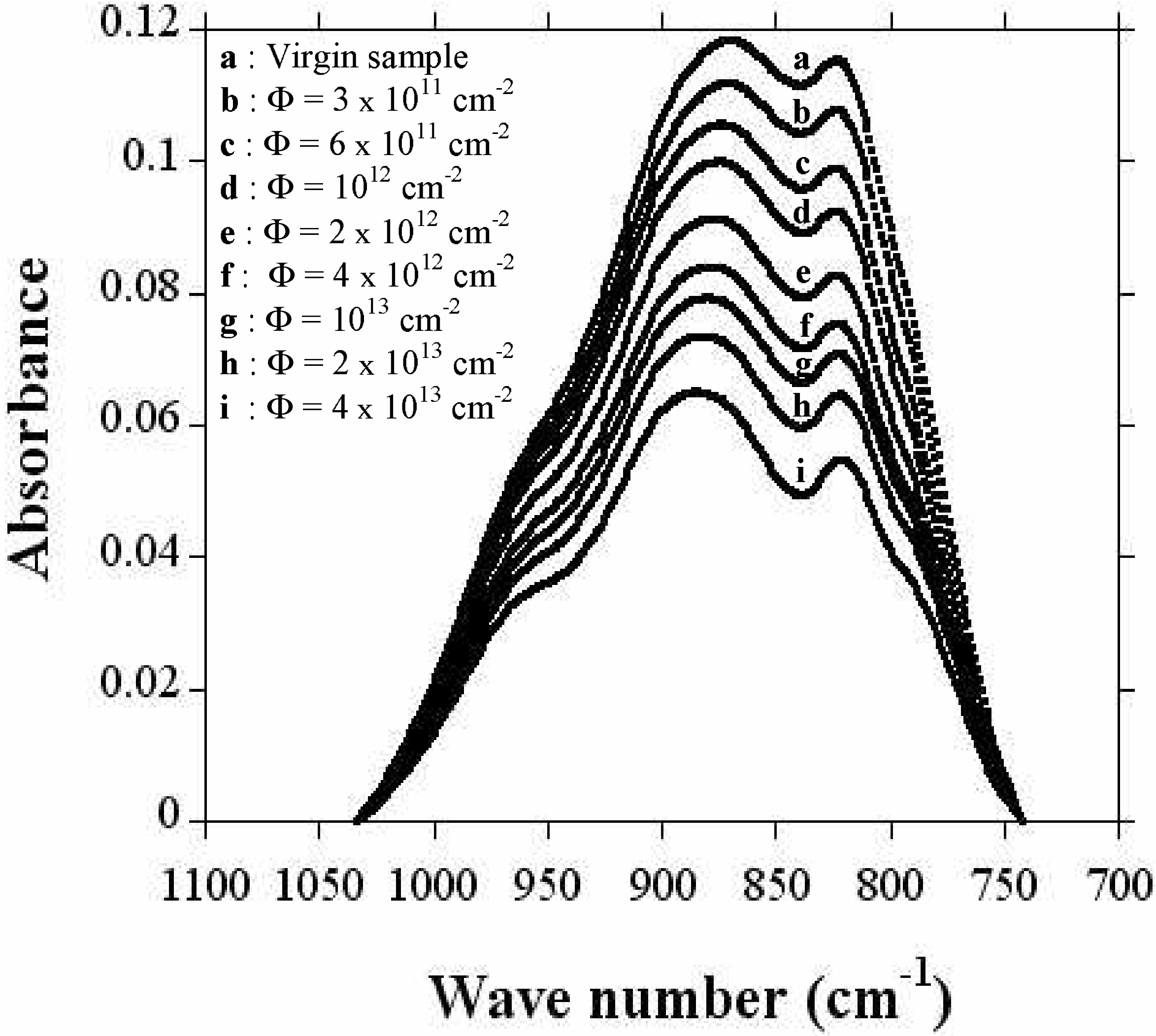
a : Virgin sample
b : $\Phi = 3 \times 10^{11}$ cm^{-2}
c : $\Phi = 6 \times 10^{11}$ cm^{-2}
d : $\Phi = 10^{12}$ cm^{-2}
e : $\Phi = 2 \times 10^{12}$ cm^{-2}
f : $\Phi = 4 \times 10^{12}$ cm^{-2}
g : $\Phi = 10^{13}$ cm^{-2}
h : $\Phi = 2 \times 10^{13}$ cm^{-2}
i : $\Phi = 4 \times 10^{13}$ cm^{-2}
a
b
c
d
e
f
g
h
i
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
1100
1050
1000
950
900
850
800
750
700
Wave number (cm^{-1})

Figure 1

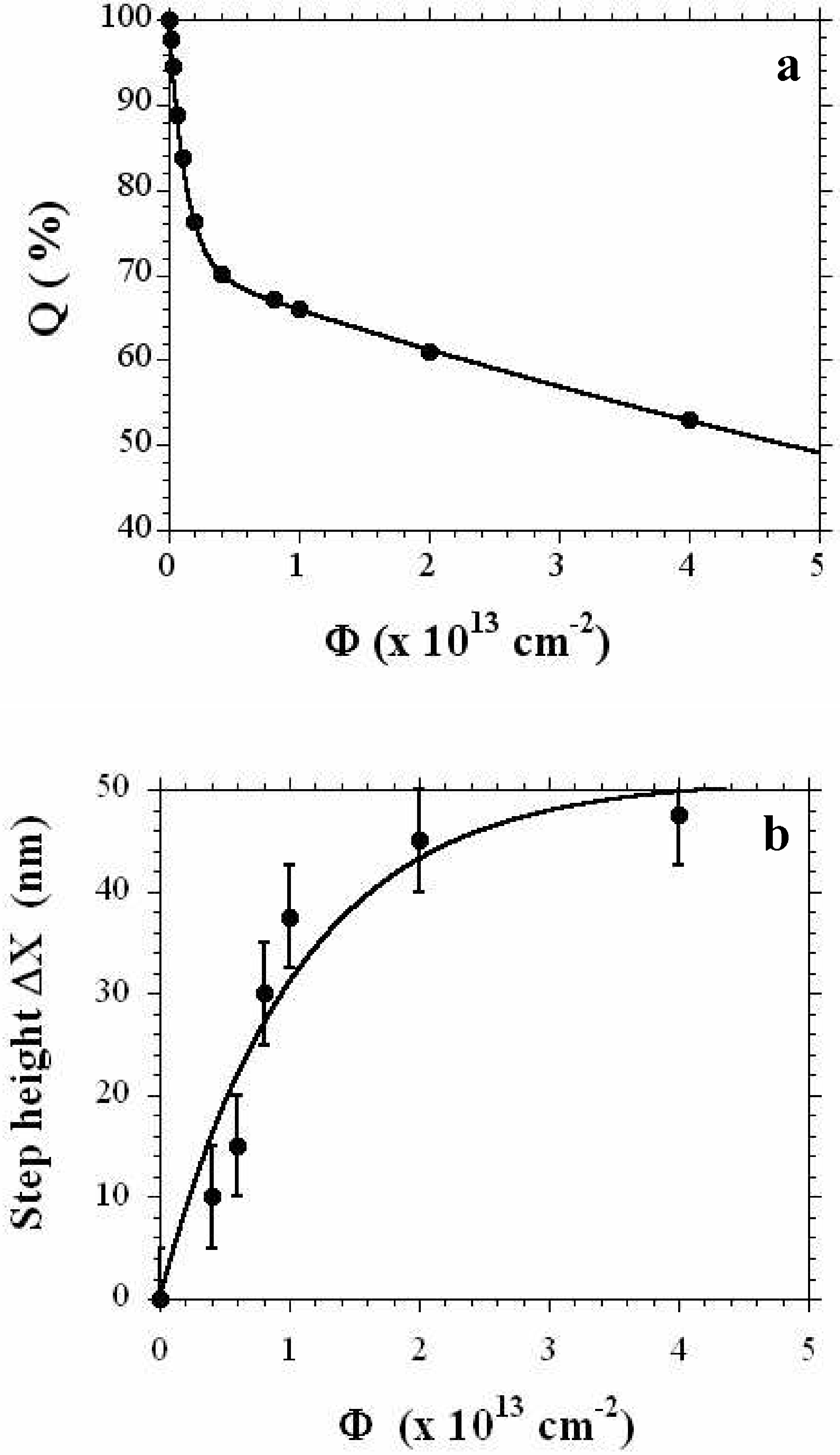
a
Q (%)
100
90
80
70
60
50
40
0
1
2
3
4
5
Φ (x 10^13 cm^-2)
b
Step height ΔX (nm)
50
40
30
20
10
0
0
1
2
3
4
5
Φ (x 10^13 cm^-2)

Figure 2

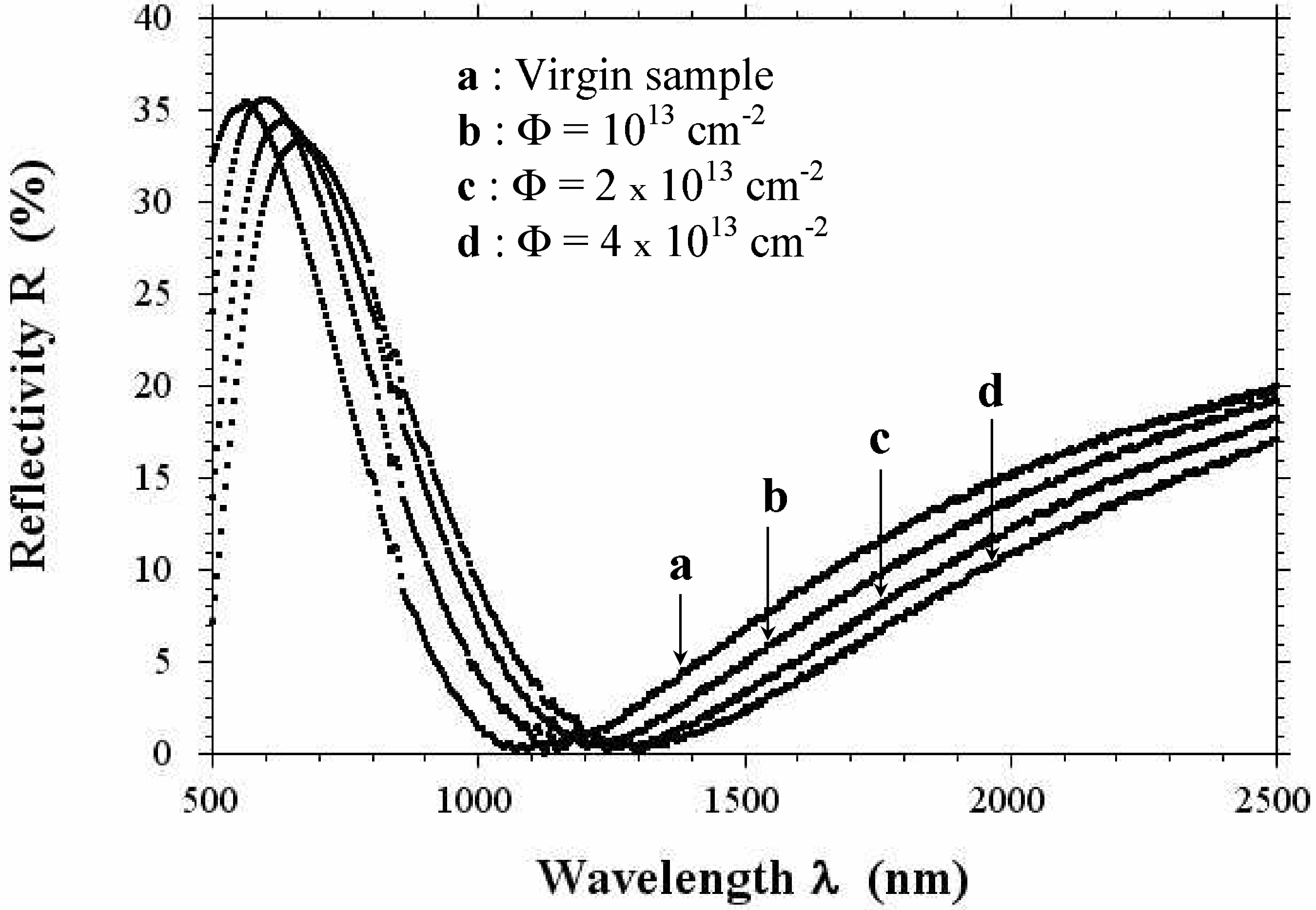
a : Virgin sample
b : $\Phi = 10^{13}$ cm^{-2}
c : $\Phi = 2 \times 10^{13}$ cm^{-2}
d : $\Phi = 4 \times 10^{13}$ cm^{-2}
a
b
c
d
Reflectivity R (%)
0
5
10
15
20
25
30
35
40
Wavelength λ (nm)
500
1000
1500
2000
2500

Figure 3

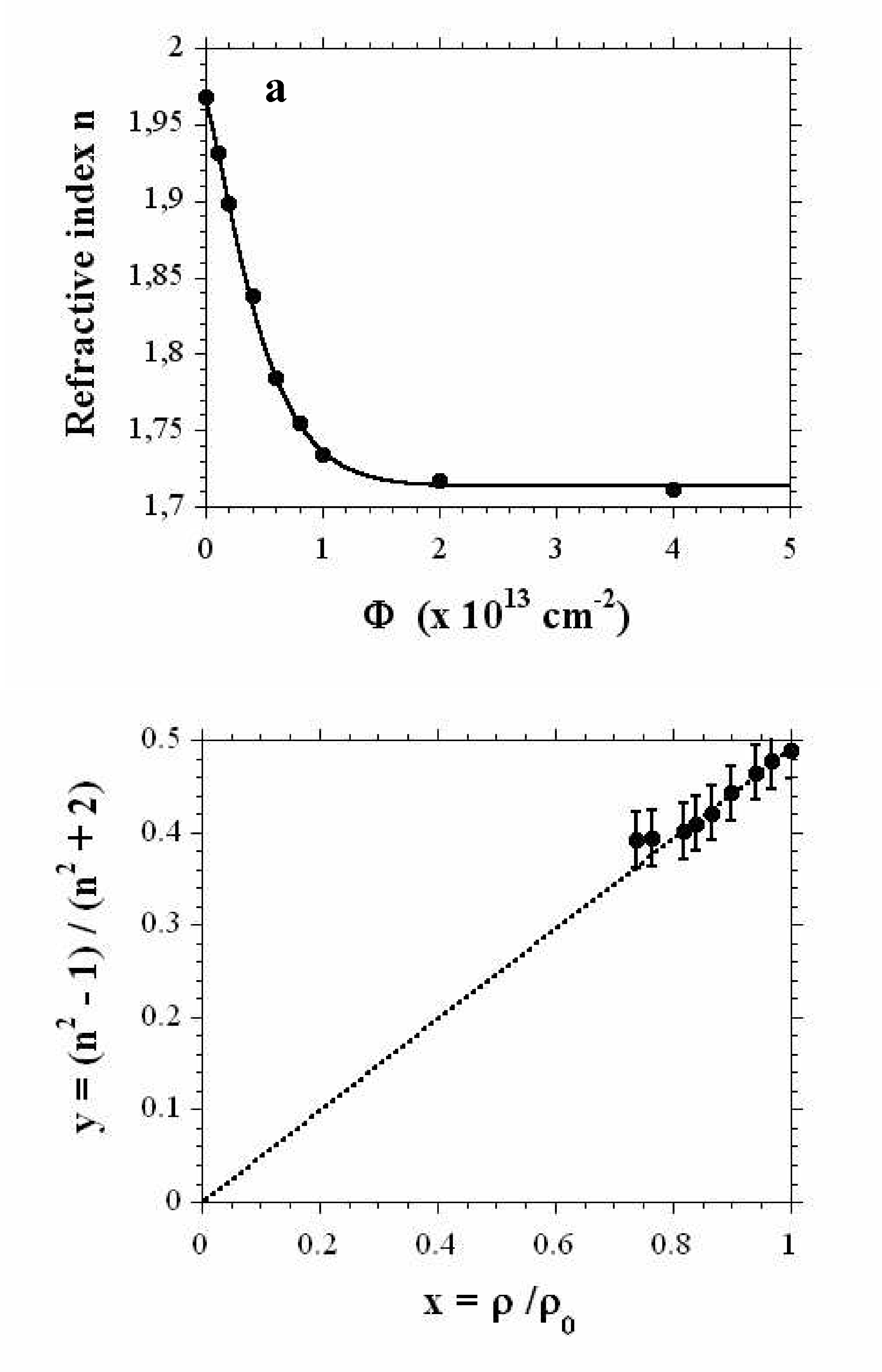
a
Refractive index n
2
1,95
1,9
1,85
1,8
1,75
1,7
0
1
2
3
4
5
Φ (x 10^13 cm^-2)
y = (n^2 - 1) / (n^2 + 2)
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
x = ρ /ρ_0

Figure 4