Phosphorous characterization and quantification in CVD SiO2(P,B)/SiO2/si multilayer system by low energy PIXE

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On the Phosphorus Characterization in Thin SiO2(P, B) CVD Layer Deposited onto a Silicon Substrate by PIXE

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ABSTRACT

In this work the capability of the PIXE technique to monitor a rapid and accurate quantification of P in thin SiO_2 (P, B) CVD layers (400 nm) deposited onto silicon substrate is discussed. In order to improve the sensitivity for P determination, a systematic study was undertaken using protons and helium ion beams at different energies using different thickness of Kapton X-ray absorbers. 600 keV proton or 1.5 MeV helium under normal incidence, using 146 μm kapton as X-ray absorber, permits an accurate quantification of P with high sensitivity within few minutes of acquisition time. This sensitivity is highly improved when using grazing incidence angles (e.g. 80°), thus 1 MeV protons can be easily used. Finally, the PIXE results shows that the phosphorus concentration in the CVD layer varies linearly with the percentage of the phosphine gas used in the CVD gas mixture.

Keywords : ***PIXE, Low Energy PIXE, CVD, Phosphorus, SiO_2, Thin layers***

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1. INTRODUCTION

Borophosphosilicate glass is an important component of silicon based semiconductor technology. The main function of such material is an interlevel dielectric capable of filling gaps and planarizing local interlevel surfaces.

The realization of ohmic contacts through a thin SiO_2 interlevel dielectric layer, via holes of few micrometers diameter, passes first by chemical abrasion. The quality of ohmic contact is highly connected to the mechanical properties of the SiO_2 layer. In fact, the edge of these holes should be as round as possible to avoid mechanical breaking. The plasticity of SiO_2 is highly improved by adding boron and phosphorus using, in general, Chemical Vapor Deposition (CVD) process. The quantification of phosphorus and boron in such devices is crucial to understand surface properties and interfacial mechanical behaviour of the deposited layer. The mechanical behaviour of the CVD SiO2 (P, B) layer, for a fixed amount of boron, is very sensitive to the phosphorus concentration.

The characterization of phosphorus in silicon matrix is, in general, not an easy task from the analytical point of view. Usually, the concentration of phosphorus in such materials is very low. This precludes the accurate determination of this element by RBS due to the interference of the silicon matrix **[1,2]**. In the same way, in the case of the Static Secondary Ion Mass Spectrometry (SSIMS) technique, the interference of silicon poses serious limitations for unambiguous surface phosphorus analysis **[3]**. In this field, the NRA technique seems to be promising and it was recently used to simultaneously quantify P and B using (α, p) reaction in thin borophosphosilacate glass films **[1]**.

In charged particle excitation, the main background contribution in the X-ray spectra is the bremsstrahlung from the secondary electrons produced in the target by the impinging ions.

The generated background gives rise to a significant background signal in the X-ray spectrum, with a maximum at the lowest detectable X-rays energy, followed by a roughly exponential decrease **[4]**. This background severely limits the detection sensitivity for elements with low atomic number. Furthermore, for a given incident ion, the bremsstrahlung decreases with its energy, much higher than the cross-section for inner shell ionization **[5]**.

Thus, Low Energy PIXE (LE-PIXE) using protons of less than 1 MeV energy or alpha particles of less than 2 MeV energy could enhance significantly the peak to background ratio for light elements. It seems to be a very powerful and sensitive technique for the characterization of elements of $Z < 20$ in surface and near surface regions **[5-8]**. In a recent review, J. Miranda **[8]** discussed the different aspects of the use of the LE-PIXE technique (advantages, drawbacks and applications).

In this paper we report, using the PIXE technique, on the experimental optimum conditions for the determination of the phosphorus concentration in thin SiO2 (P, B) CVD layers deposited onto intrinsic silicon substrates. In this way, the PIXE parameters (ion type, energy, X-ray absorber and incidence angle) were optimized in order to have an acceptable compromise between sensitivity and acquisition time. Consequently, we should monitor phosphorus concentration in the CVD layer versus the partial pressure of the phosphine gas in the CVD reactor gas mixture.

2. EXPERIMENTAL

2.1 Samples

In a reactor filled with silane gas, mixed with a few percent of phosphine and borane, the CVD samples were deposited onto 7.5 cm diameter intrinsic silicon wafers, 0.1 mm thick, covered with ~ 100 nm thermal oxide to prevent self-doping. The percentage of the phosphine

gas in the CVD gas mixture varies from 0 to 4 % (0, 2, 3, 3.5 and 4 %) while the one of borane was fixed at 3.5 % in all prepared samples. The thickness of the CVD deposited layer was ~ 400 nm measured by ellipsometry and checked by RBS.

The wafer was cut to fit the 10-mm size of the Al sample holder diameter and cleaned with analysis grade acetone followed with bidistilled water. In order to ensure good electrical contact with the Al frame the analyzed surface was glued using double side carbon tape.

2.2 PIXE instrumental set-up and data analysis

Proton (0.5 - 3 MeV energy) and helium (1 - 3 MeV energy) beams were delivered by the 1.7 MV 5-SDH NEC Pelletron tandem accelerator of the Lebanese Atomic Energy Commission. The beam intensity range was between 5 and 80 nA. The spot diameter of the beam, on the target, was about 2-4 mm, defined by a Ta antiscatter collimator. At ~ 15 cm prior to the beam entry in the analysis chamber, a quaetz equipped by a CCD camera allows to control the beam alignement and its focusing. The in vacuum PIXE scattering chamber which contains X-ray and surface barrier particle detectors (SBD), is equipped with a wheel target holder (up to16 samples) monitored by PC. X-ray emission from targets was detected using an Ortec Si(Li) detector (SLP-06165 model) with 30 mm² active area, 12.7 µm thick Be window and 170 eV measured FWHM energy resolution at 5.9 keV, situated at 135° referring to the beam direction. The distance between the target and the Si(Li) detector was ~ 4 cm. Kapton® filter, used as X-ray absorber, with various thickness values (131 and 146 µm), was inserted between the sample and the detector in order to improve the system's efficiency for phosphorus detection. The beam current, on the target, is measured via a 20 cm length graphite faraday cup electrically isolated from the analysis chamber and situated in the beam direction at ~ 1 cm behind the target. An Ortec charge integrator, connected to an Ortec digital counter-timer, measures the beam charge deposited on

the target. In order to have an accurate measurement of the charge secondary electrons suppression was realized by putting the target between two appropriate aluminum wires biased at – 400 Volts. The bias voltage was optimized in order to have less than 1 % difference between the current measured directly by the Faraday cup (without sample) and the one measured through the sample. This procedure was controlled by an RBS charge monitoring, simultaneously with the PIXE, using a variety of Micromatter® thin film standard materials. The used particle detector was a SBD Canberra with a 50mm² active area and a measured energy resolution, for protons, of ~ 12 keV at FWHM.

The detectors were connected to a multiparameter system, allowing simultaneous acquisitions, through a conventional electronic chain using standard NIM electronic models.

The X-ray spectra were, in off line mode, analyzed with the GUPIX computer code **[9]**. Prior to measurements, operational parameters of the program were determined by measuring a set of 31 Micromatter thin film standard materials deposited onto nucleopore substrates covering 35 elements with an X-ray range from 1,25 to 35.5 keV. In addition, SRM 1832 and SRM 1833 standard reference materials (thin glass films deposited onto thin polycarbonate backing) were used as quality control. Finally, the X-ray count rate was <1000 Hz and the dead time, in all measurements, was ~ 0.5 %. The energy loss calculations were obtained using the TRIM code **[10]**.

3. RESULTS AND DISCUSSION

3.1 Energy and filter optimization under normal incidence

In order to improve the sensitivity of the PIXE technique, for the determination of phosphorus concentrations in the CVD SiO2 (P, B) layer, we should consider different energies of the incident particle, either for proton or for alpha, as well as different thickness values of the

selected X-ray absorber (e.g. kapton filter). The main features of this study may be discussed referring to Fig.1, which shows the variation of the yield ratio Y_P/Y_{Si} versus the energy of the incident particle, for two different thickness values of kapton filter. It shows also the variation, versus energy, of the ratio between the K shell X-ray emission cross section of phosphorus and the one of silicon.

If Y_P is the calculated phosphorus K X-ray yield, to be detected by our Si(Li) detector, for a given phosphorus concentration (e.g. 2.5 %) in the 400 nm SiO2 (P, B) CVD layer, and Y_{Si} is the silicon calculated K X-ray yield over the total emission depth in the multilayer system, so these yields can be expressed as:

$Y_P = Y_{tot}$ [P, Kα] ζi[[P, Kα] ε[P, Kα] Ω

and

$Y_{Si} = Y_{tot}$ [Si, Kα] ζi[Si, Kα] ε[Si, Kα] Ω,

Y_{tot} is the total K_α X-ray emitted from the target, either for P or Si, at a given incident particle energy, ζi is the transmission coefficient factor for a given X-ray absorber with a given thickness value, ε is the detector efficiency, for P or Si K X-ray energy and Ω is the detection solid angle. The calculations of Y_{tot}, ζ_i, ε, σ_k(P) and σ_k(Si) were performed using Guyls and Gucsa routines of the GUPIX code.

Fig.1 shows clearly that:

1) The sensitivity for the phosphorus determination, which is directly proportional to the Y_P/Y_{Si} ratio, increases with the decreasing of the incident particle energy. This is mainly connected to the analyzed depth of the incident particle, at a given energy, and not to the X-ray production cross section ratio between P and Si.
2) This sensitivity increases also with increasing thickness value of the X-ray filter for a given energy and for a given incident particle. This is due, evidently, to the transmission

coefficient factors ratio between P and Si.

3) For protons, Y_P/Y_{Si} starts to increase significantly for Ep < 1 MeV.
4) The use of alpha particles, which have smaller penetration depth than protons at the same energy, will be useful for obtaining a good sensitivity in the determination of phosphorus concentration in the CVD layer, at relatively low energies (≤ 2 MeV).

In practice, necessary acquisition time to obtain good statistics should be taken into consideration. This time is mainly related to the X ray production cross section, for a given energy and a given incident particle, to the X-ray attenuation factor, for a given X-ray absorber thickness and to the current beam intensity which depends on the beam energy. For this purpose, a systematic study was undertaken in order to have the optimized energy and filter thickness, either for proton or helium beams. Among our set of samples, the optimization of experimental parameters was performed using logically the sample that was prepared with the lowest partial pressure of phosphine (2 %) in the CVD gas mixture. Our results showed that a 600 keV proton beam and 1500 keV alpha beam, with 146 μm Kapton, are good enough parameters for the determination of phosphorus concentration in the CVD layer, with relatively high sensitivity and within 20-30 minutes acquisition time. To resume, figure 2 shows the PIXE spectra of the analyzed 2% phosphine sample using proton beam at 2.5, 1 and 0.5 MeV. It can be shown that the use of the conventional PIXE, using protons of 2-4 MeV energy, gives rise to a huge silicon signal growing on a huge bremsstrahlung background and consequently the phosphorus detection is at its worse. At lower energies, the phosphorus signal starts to contribute more and more to the integral X-ray spectrum due to: (i) lower bremsstrahlung effect and (ii) decreasing information depth. Figure 3 presents the PIXE spectra of the same sample using He beam at 2.5, 2 and 1.5 MeV. In this case, the improvement of the P signal detection is mainly related to a decrease in

the penetration depth at the lowest energy (1.5 MeV).

3.2 Phosphorus concentrations versus % of phosphine in the CVD gas mixture

The determination of phosphorus concentrations in the various CVD samples was done using the optimized conditions discussed above. 600 keV proton and 1.5 MeV helium ion beams were used at normal incidence. In both cases, 146-μm thickness of kapton X-rays absorber was used. Using a beam current of around 80-100 nA, good statistics for phosphorus determination can be achieved for a total charge of 150 μC, within ~ 20-30 minutes acquisition time. In this case, for the lowest concentration (2% phosphine), the net area of the phosphorus peak was ~3000 counts and the limit of detection (LOD) of phosphorus was ~ 850 – 900 ppm. In order to check the homogeneity of the CVD layers, the analysis of different samples, from the same wafer, was performed and showed very similar results with variations ranging between 3 and 5%. The precision of the measurements was ~ 3 %.

Fig.4 shows the variations, in the case of helium and hydrogen beams, of the phosphorus concentrations in the SiO2(P,B) CVD layer versus the percentage of the phosphine gas in the CVD gas mixture. These concentrations were calculated in two different ways:
(i) in μg/cm2, when the CVD layer is considered as thin. Thus, the energy loss of the incident ion, in the considered layer, as well as the self absorption of the phosphorus X- rays en route to the target surface, are negligible and (ii) in ppm, where the above neglected parameters are taken into account, in the GUPIX calculations, and thus the CVD layer is considered as intermediate target.

Referring to Fig.4 one can see that, besides the precision, there is no discrepancy between the results obtained using He or proton in the case of intermediate target. In contrast, a significant discrepancy exists between the results obtained with the thin layer approach where

the obtained concentrations are underestimated in the case of helium beam. This can be explained by a non negligible energy loss, in the CVD layer, for 1500 keV helium beam, which did not occur in the case of proton beam. In fact in the considered SiO2 layer of ~117 μg/cm², the energy loss using 600 keV protons is about 30 keV while in the case of 1500 keV helium the energy loss is around 160 keV. This can give rise to a difference in the phosphorus K-X ray production cross section, between the energy of the incident ion at the surface and its energy at the CVD layer-silicon substrate interface. This difference is about 30% in the case of helium and less than 11% in the case of proton. Finally, the phosphorus concentration in the CVD layers varies linearly with the percentage of the phosphine gas and can be expressed, within less than 7 % precision, as [P]=1.55[%Phosphine] with a correlation coefficient $r^2 = 0.985$. The [P] can be either in ppm or in μg/cm².

3.3 Surface phosphorus sensitivity versus target tilting angle

An alternative technique to the incident particle energy variations, for PIXE surface analysis, is the tilting of the sample with respect to the beam direction which allows to modify the apparent thickness of the layer crossed by the incident beam **[11,12]**. In this way, for a given proton energy, the sensitivity for surface phosphorus determination increases with increasing of the tilting angle (φ) since X-ray yield is inversely proportional to cosφ. Fig.5 presents the experimental variations of the phosphorus yield in counts/μC and the variations of the LOD versus the target tilting angle, for protons at 0.6 and 1 MeV in the case of the 2% phosphine CVD sample. The LOD decreases significantly between 60° and 80° target tilting angle (factor of ~ 2). In the same way, for a given proton energy, the sensitivity for phosphorus determination increases rapidly from a tilting angle > 60°.

Fig.6 shows the PIXE spectra at 80° target tilting angle, for the 2% phosphine CVD

sample, obtained under 0.6 and 1 MeV proton, using 146-µm kapton X-rays absorber. In comparison with normal incidence beam, the Y_P/Y_{Si} ratio is highly improved ~ 0.52 (at 1 MeV) and ~1.37 (at 600 keV) against ~ 0.12 and ~ 0.20 respectively in the case of normal incident proton beam. In addition, the phosphorus signal to background ratio (Sp/B) at 80° tilting angle was found ~1.1 against ~ 0.3 under normal incidence for 600 keV proton and ~ 0.6 against ~ 0.12 for 1 MeV protons. From these results it can be seen that at grazing angle, 1 MeV proton gives significantly higher sensitivity for phosphorus determination than 600 keV protons under normal incidence. Consequently, using 1MeV protons at 80° tilting angle, good statistics for phosphorus determination can be obtained within few minutes. In addition, grazing angle experiments were also done for Ep > 1 MeV and (Sp/B) was found to be rapidly dropped and the phosphorus was hardly detectable.

Beside P and Si, the peaks showed in the spectra (Cl, K, Ca and Fe) were not detected for the same sample under normal incidence. The cleaning procedure, given in the experimental section, is not enough to remove the surface contamination present at very low concentration levels (< 10 ng/cm²). This can be due to a residual accidental contamination of the CVD reactor.

4. CONCLUSION

In this work, it has been demonstrated that the Low Energy PIXE is an accurate, rapid and powerful technique for phosphorus quantification monitoring, in the percent level, in thin CVD SiO2(P,B) layer deposited onto silicon. In the present study, it was found that, under normal incidence, 600 keV proton energy and 1.5 MeV helium energy using 146 μm kapton X-rays filter represent a good compromise for a rapid quantification of phosphorus (< 30 minutes) with relatively high sensitivity with a LOD < 900 ppm. With 80° tilting angle, conventional PIXE using protons at 1 MeV can be used for rapid quantification (few minutes) of the phosphorus with relatively high sensitivity (Sp/B ~0.6) and LOD of ~ 500 ppm. The 400 nm SiO2 CVD layer could be considered as thin target for proton beam even at lower energy (500-600 keV), while for accurate quantification of phosphorus using He beam at 1.5 MeV, an intermediate target approach should be considered for energy loss and X-rays self absorption corrections. Finally, the concentration of P shows linear dependence with the percentage of phosphine in the CVD gas mixture.

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REFERENCES

[1] D.S. Walsh and B.L. Doyle, Nucl. Instr. and Meth. in Phys. Res. B 161-163 (2000) 629

[2] H. Allali, PhD Thesis, Université Claude Bernard Lyon I (1993).

[3] H. Allali, B. Nsouli, J.P. Thomas, W. Szymzack and K. Wittmaack, Nucl. Instr. and Meth. in Phys. Res. B 90 (1994) 501.

[4] F. Folkmann, C. Gaarde, T. Huus and K. Kemp, Nucl. Instr. and Meth. in Phys. Res. 116 (1974) 467.

[5] K. Wittmaack and B. Hietel, Nucl. Instr. and Meth. in Phys. Res. B161-163 (2000) 814.

[6] F.M. El-Ashry, M. Goclowski, L. Glowacka, M. Jaskola, J. Marczewski and A. Wolkenberg, Nucl. Instr. and Meth. in Phys. Res. B 22 (1987) 450.

[7] C. Neelmeijer, I. Brissaud, T. Calligaro, G. Demortier, A. Hautojörvi, M. Mäder, L. Martinot, M. Schreiner, T. Tuurnala and G. Weber, X-Ray Spectrom. 29, (2000) 101.

[8] J. Miranda, Nucl. Instr. and Meth. in Phys. Res. B118 (1996) 346.

[9] J.A. Maxwell, J.L. Campbell and W.J. Teesdale, Nucl. Instr. and Meth. in Phys. Res. B43 (1989) 218.

[10] J.F. Ziegler, J.P. Biersack and U. Littmark, The Stopping and Ranges of Ions in Solids, Pergamon, New York, 1995.

[11] G. Weber, J.M. Delbrouck, D. Strivay, F. Kerff and L. Martinot, Nucl. Instr. and Meth. in Phys. Res. B139 (1998) 196.

[12] L. Rodriguez-Fernandez, W.N. Lennard, G.R. Massoumi, H. Xia, L.J. Huang, Y. Hung and S. Chang, Nucl. Instr. and Meth. in Phys. Res. B136-138 (1998) 1191.

FIGURE CAPTIONS

Figure 1: Variations of Y_P/Y_{Si} (see text) versus incident particle energy for hydrogen beam using 131 μm and 146 μm kapton X-rays absorbers and for helium beam using 146-μm kapton X-rays absorber. The variations of the K X-ray production cross section ratio between phosphorus and silicon [σkx(P)/σkx(Si)] are shown for comparison (same scale as Yp/Ysi yields ratio).

Figure 2: PIXE spectra of the 2% phosphine CVD sample obtained using 146 μm thick kapton X-rays filter under proton bombardment at: (a) 2.5 MeV, (b) 1 MeV and (c) 0.5 MeV.

Figure 3: PIXE spectra of the 2% phosphine CVD sample obtained using 146 μm thick kapton X-rays filter under alpha particle bombardment at (a) 2.5 MeV, (b) 2 MeV and (c) 1.5 MeV.

Figure 4: Variations of the phosphorus concentration in the CVD SiO_2(P,B) layer versus the percentage of the phosphine gas in the CVD gas mixture. The variations are calculated for both hydrogen and helium beam. The P concentration is given in μg/cm², in the case of thin target calculation, and in percentage in the case of intermediate target calculation (same scale).

Figure 5: Experimental variations of the P(LOD) in ng/cm², and P(counts/μC) versus the tilting angle of the 2% phoshine sample, for 0.6 MeV and 1 MeV.

Figure 6: PIXE spectra of the 2% phosphine CVD sample obtained using 146 μm thick kapton X-rays filter under 80° tilting angle and using protons at: (a) 1 MeV, (b) 0.6 MeV.