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New profiled Silicon PIN Photodiode for Scintillation Detector

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Abstract

Silicon photodiodes (planar PIN) are employed for the read out of scintillation shower counters. We have already reported on a new doping method called molecular layer doping (MLD) which has been developed for a quarter-micron ULSI process. In this study, several types of PIN photodiodes, in which a p^+ layer was formed by MLD (MLD-PIN) or BF_2 ion implantation (BF_2 I/I-PIN), have been examined. The MLD-PIN has a shallow p^+ junction depth (x_j) with sufficient high surface concentration, and simply and easily provides good performance for a short-wavelength photo sensitivity.

I. INTRODUCTION

Currently, silicon photodiodes (planar PIN) are employed for the read out of scintillation shower counters [1]. They are very compact, have low power consumption, and are insensitive to magnetic fields. However, they still require a high quantum efficiency within the wavelength range from 350 to 650 nm, in terms of the photoelectron collection yield for scintillation counting.

In order to increase this short-wavelength quantum efficiency, p^+ layer junction depth (x_j) at p^+-n^--n^+ PIN structure is expected to be as shallow as possible. However, forming a shallow p^+ layer while maintaining sufficient impurity surface concentration (for series resistance, contact resistance and surface state stability, >1E19 cm^{-3}) is not easy using one of the conventional processes such as the BBr_3 pre-deposition method or the B (boron, B^+) ion implantation method. It is not realistic to consider the BBr_3 pre-deposition method because of its p^+ x_j (above around 1.0 μm). Even for the B ion implantation method, around 0.5 μm is the actual minimum x_j. Because the B^+ is a light weight element thus it shows a long projected range (R_P), and has a lower ionization rate thus it needs a higher annealing temperature (above 950°C to have at least 80% impurity ion activation) which leads to deeper x_j. The BF_2 ($^{49}BF_2^+$) ion implantation was also employed to perform p^+ layer in this study. Because the R_P of BF_2 is 25% of B, and higher ionization rate (550°C annealing enough to have 80% activation, 900°C to have almost 100%). Thus the BF_2 I/I method is expected to obtain sufficient shallow x_j, however, the BF_2 implantation induces some undesirable results such as damage [2]. The BF_2 implantation causes an amorphous Si layer on the surface of Si crystal (therefore shorter R_P). This amorphous Si layer will be recrystalized by subsequent annealing. The residual interface caused by insufficient annealing between the amorphous layer and the single crystal layer is called the damage. This may cause recombination of carriers, and eventually adversely affect the photo sensitivity.

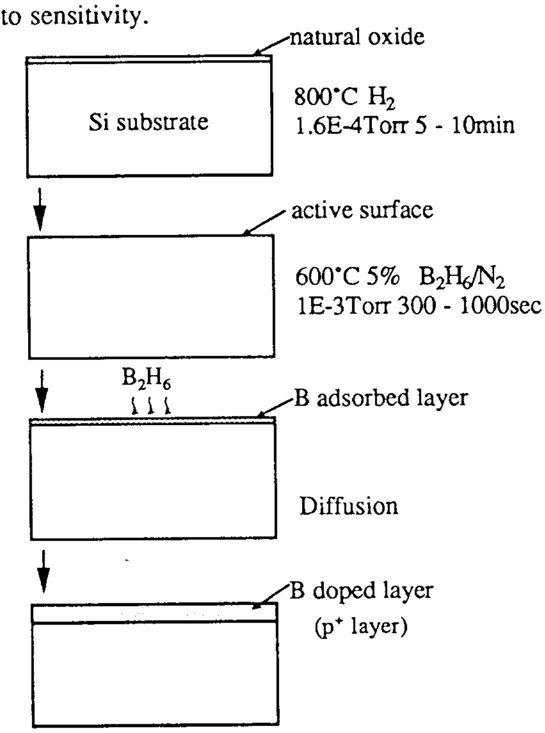

Fig. 1 MLD process steps.

On the other hand, we have already reported on a new doping method called molecular layer doping (MLD) [2, 3] which has been developed for a quarter-micron ULSI process. In this study, several types of PIN photodiodes, in which a p^+

layer was formed by MLD (MLD-PIN) or BF_2 ion implantation (BF_2 I/I-PIN), have been examined.

II. SAMPLE PREPARATION

The MLD process consists of three essential steps, as shown in Fig. 1. First, the natural oxide on the Si surface is removed by thermal cleaning to expose an active Si surface. In the second step, a boron adsorbed layer is formed on the Si surface.Third is solid phase diffusion of boron atoms, from the boron adsorbed layer, into the bulk. After that, the boron adsorbed layer is removed by thermal oxidation.

In this study, several types of PIN photodiodes, in which a p^+ layer was formed by MLD (MLD-PIN), have been examined. For comparison, other PIN photodiodes have also been examined, in which the p^+ layer was formed by ion implantation (B, BF_2 I/I-PIN). Multiple types of x_j sample within several types of substrate have been prepared by combining several lengths of doping time and several kinds of subsequent annealing in the MLD. Also, in the I/I, multiple types of x_j sample have been prepared by combing several dosages and several kinds of subsequent annealing, as listed in the following:

Si substrate:		
	Thickness	300 µm
	Orientation	<111> <100>
	Resistivity	1 - 3 kΩcm 4 - 8 kΩcm
Doping:		
	B I/I	5 - 50E14/cm^2
	BF_2 I/I	5 - 50E14/cm^2
	MLD	300 - 1000sec
Annealing:		
	N_2, 60min	800 - 1000°C

In the other processes used for forming the n^+ layer, the oxidation and metalizations were the same. There were multiple types of photo-sensitive area size, 1 x 1 mm - 10 x 20 mm. Photo sensitivity and other characteristics were measured after coating the samples with a transparent resin.

III. EXPERIMENTAL RESULTS

A. Photo sensitivity performance

Fig. 2 shows the spectral responsivity of the above PIN photodiodes:Using the sample preparation method shown above, multiple types of x_j sample have been made, several of which were represented as higher and lower photo sensitivity for each case of BF_2 I/I and MLD, without any normalized earlier. The photo sensitivity (A/W is A/W/cm^2) was calculated from a photo current obtained with 40 volt reverse bias with 100 kΩ series resistance, and with irradiation of 10 µW/cm^2 luminescence from a collimated light source (W lamp, 3200 K). The value of the photo current was arrived at through the use of a pre-adjusted light source. Therefore, although it is used as an exact value, the results of others might vary. However, the relative values contained in this study are considered to be sufficiently accurate. Every plot is the average of every 10 PINs with a deviation of only a few percent. The B (boron) I/I-PIN shows lower photo sensitivity with every sample (e.g 0.105 A/W at 1E15/cm^2, 950°C), which will be discussed concerning the BF_2 I/I-PINs and MLD-PINs in the following sentences. Fig. 3 shows the relationship between photo sensitivity at 400 nm and p^+ layer junction depth (x_j) obtained by SIMS (Secondary Ion Mass Spectroscopy). The MLD-PINs show a clear increase in the photo sensitivity at short wavelength (400 nm), with x_j becoming shallow. The BF_2 I/I-PINs do not show simple x_j dependence.

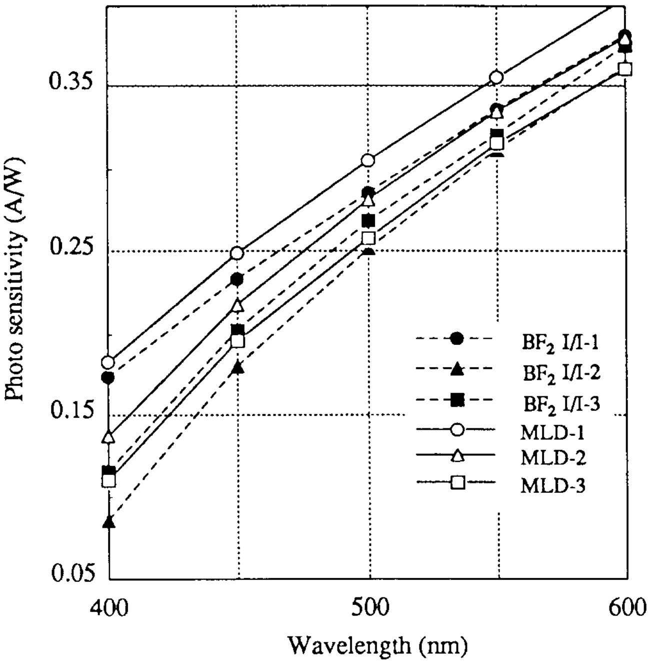

Fig. 2 Spectral responsivity of MLD-PIN and BF_2 I/I-PIN.

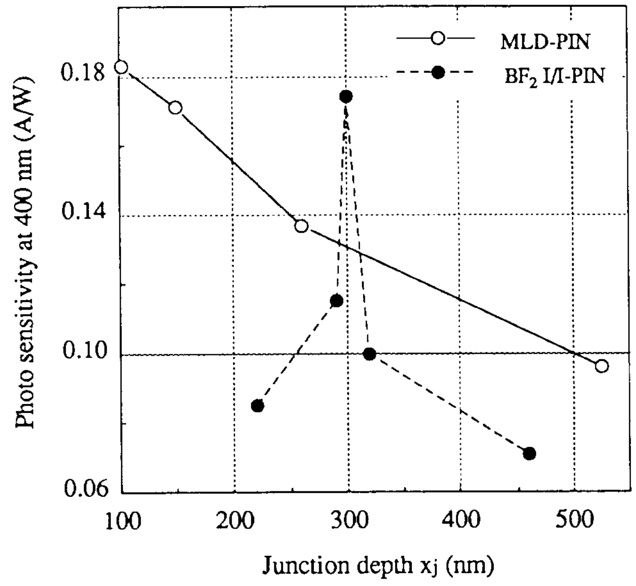

Fig. 3 Junction depth versus photo sensitivity at λ=400 nm wavelength.

This can be explained as follows. The BF_2 I/I-PINs were affected by the damage which was caused by ion implantation as mentioned above. As the temperature rises, damage will be eliminated, however, x_j will deepen further, and mechanisms, in which the sensitivity dose not rise, have complex combinations under each condition.

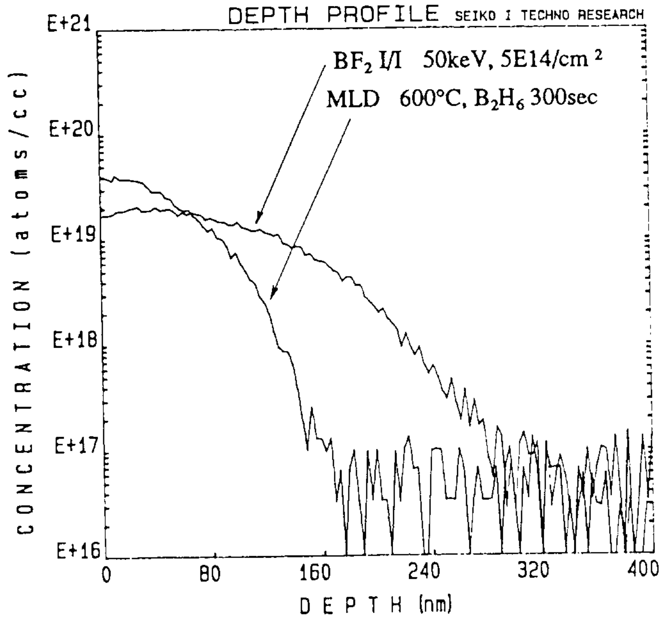

Fig. 4 Boron profile by SIMS.

Fig. 4 shows a boron profile by SIMS. The MLD-PIN has a shallow p^+ x_j with sufficient high surface concentration as we expected.

B. Process dependences

Fig. 5 shows the relationship between annealing temperature and photo sensitivity under one doping condition of each PIN. This graph can more easily explain the complex data of BF_2 I/I-PINs, described above. If there is increase in the annealing temperature below 1000°C, there is an increase in the photo sensitivity of BF_2s. This can be explained by damage (as mentioned above) restoration. At 1000°C annealing, there is a decrease again in sensitivity which can be attributed to a deepening of x_j. This suggests that an increase in the annealing temperature is proportional to a decrease in the photo sensitivity of the MLDs. At 950°C annealing, the BF_2s shows higher photo sensitivity than that of the MLDs in spite of almost the same depth of the x_j. Higher photo sensitivity might be expected at 800°C for the BF_2s, if the damage restoration occurs without a deepening of x_j.

Because of its high resolution (1E11/cm^2) for monitoring the ion implantation dosage, the thermal waves method [5] has been extensive use recently in the field of semiconductor manufacturing. Thermal waves signal (TW signal) is useful to estimate the damage density as well as impurity dosage. Fig. 6 shows the TW signal at each point along the process. Each plot of the TW signal is completely stable, but, again, there is a deviation of a few percent. Although the "as dope" signal of the BF_2 90,000, the scale of the vertical axis of the graph is not log, but linear in terms of the characteristics of the TW signal. The TW signal was measured with a Therma-Probe 400xp made by Therma-Wave, Inc.

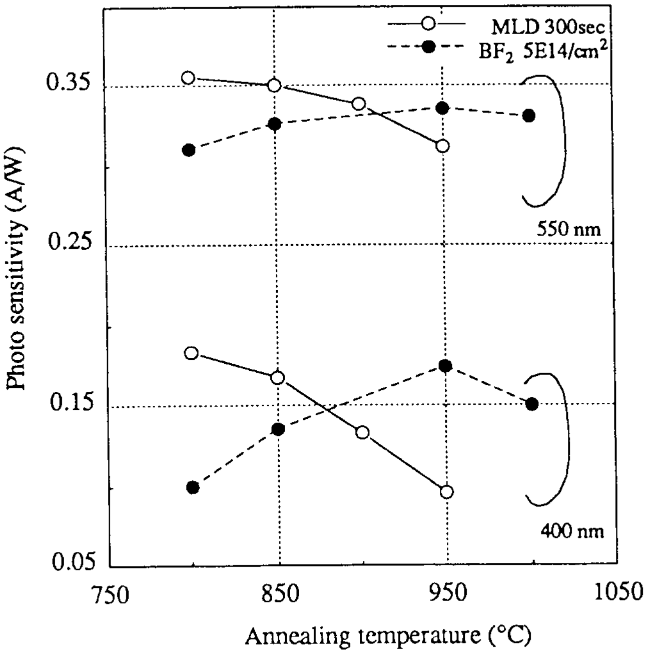

Fig. 5 Annealing temperature versus photo sensitivity.

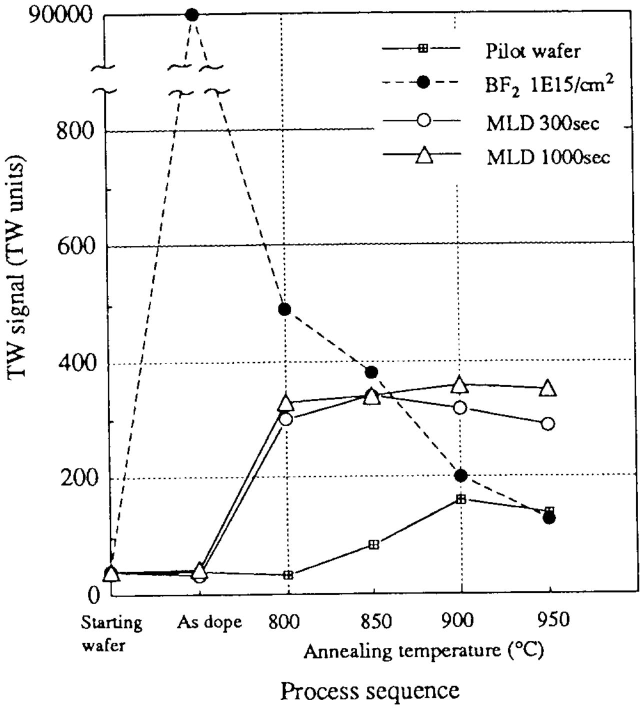

Fig. 6 Process sequence versus thermal waves signal.

The signal of the BF_2 shows the expected damage restoration (recrystalization), whereas, the MLD signal reveals some interesting tendencies. At first, the MLDs show no increase of signal at the point of "as dope" (the MLD signal was measured after the boron adsorbed layer was removed); and, once the increase in the thermally processed TW signal appeared and it is stable, there was no dependence on the annealing temperature or MLD deposition time (the quantity of boron). Assuming this signal is the damage of the MLD method, above 850°C turned by TW signals of BF_2s in terms of the density of the damage. This can possibly explain Fig. 5 also, if it plays the role of damage.

C. Detection of scintillation

The spectra of ^{137}Cs and ^{60}Co was detected with PINs fabricated in this study, using the CsI (Tl) scintillator. The characteristics of the BF_2 I/I-PIN are photo sensitivity of

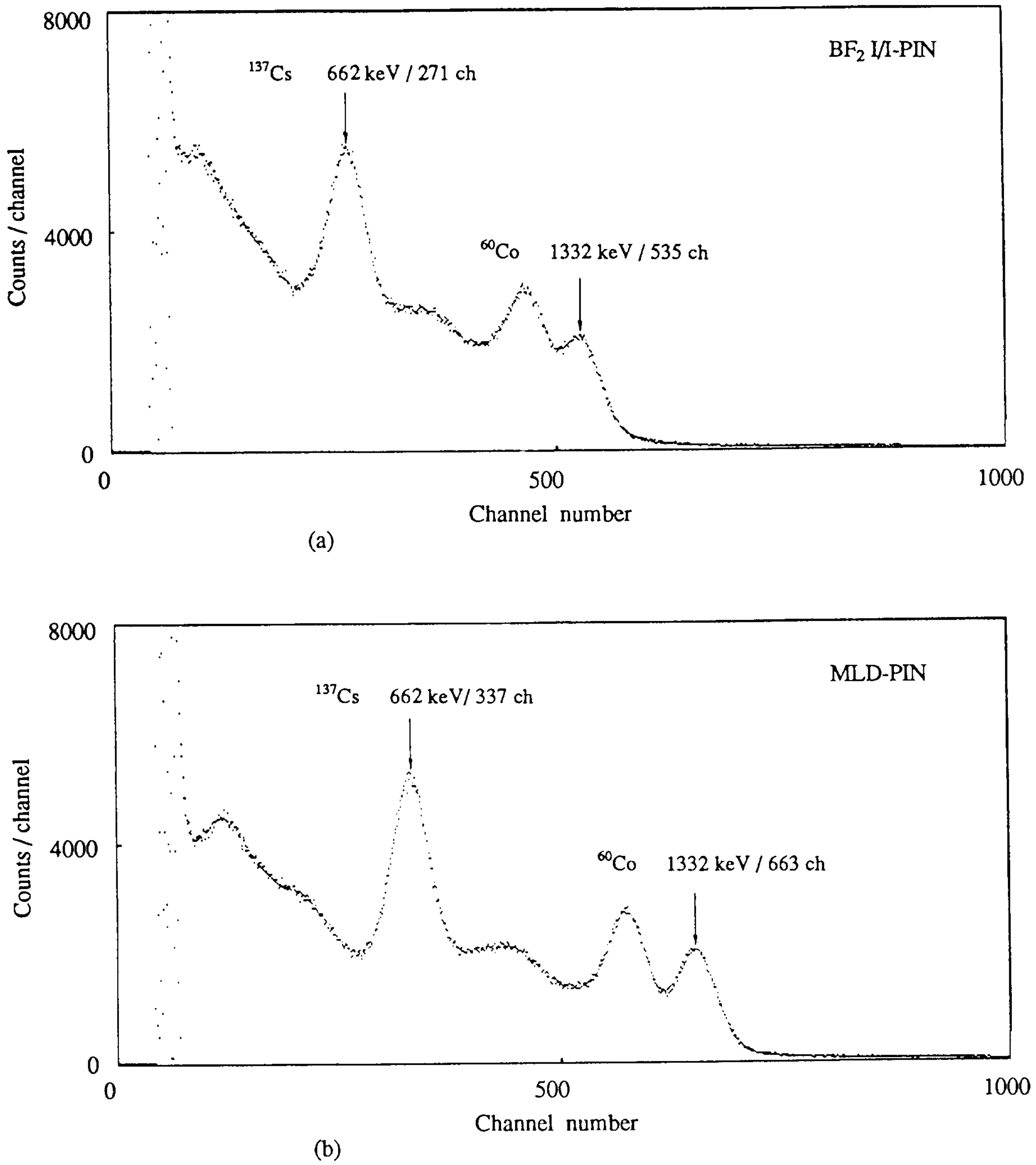

Fig. 7 ^{137}Cs and ^{60}Co spectra detected with BF_2 I/I-PIN (a), and MLD-PIN (b).

0.174 A/W at 400 nm, and 0.336 A/W at 550 nm, junction capacitance of 83.7 pF at full depletion voltage of 50 V, and a leakage current of approx 4 nA at 50 V at 25°C, area size 1 x 2 cm. Those of the MLD-PIN are 0.183 A/W at 400 nm, 0.356 A/W at 550 nm, 84.6 pF at full depletion voltage of 40 V, and a leakage current of approx 4 nA at 40 V at 25°C , area size 1 x 2 cm. As described above, both sample have sufficient performances for a scintillation counting, such as the low capacitance, the low leakage current and the enough depletion width, as well as the photo sensitivity. The scintillator was a 1 inch cubic CsI(Tl) crystal, the power supply was a KEITHLEY 617, the preamplifier was a CLEAR PULSE 580, the shaper was a ORTEC 672 (gain: 300, shaping time: 2 μsec), the MCA was a ORTEC 917 (conversion gain: 1 k ch), and the controller was a PC9801 with an emulation program by SEIKO EG&G.

Fig. 7 shows the measured results, the spectra of ^{137}Cs and ^{60}Co, and the energy peak for each channel. The spectra of the BF$_2$ I/I-PIN shows almost the same shape and the same peak position for the current typical photodiode [1] measured at the same time. The spectra of the MLD-PIN shows higher relative peak position for the channel than that of the BF$_2$ I/I-PIN, thus it shows clearer peak resolution and lower tailing (lower noise). Within this measurement, the energy efficiency of the relative peak position for each channel was estimated that the value of the MLD-PIN is higher than that of the BF$_2$ I/I-PIN. The wavelength of maximum emission of CsI(Tl) is around 560 nm, those of BGO or CdWO$_4$ is around 480 nm. Further effective scintillation counting is expected with MLD-PINs.

IV. DISCUSSION

In this study, several kind of significant data were obtained, such as the short wavelength photo sensitivity process dependences or scintillation counting performances, for the PIN photo diode in which p$^+$ layer was formed by MLD or B or BF$_2$ ion implantation, as we expected.

Particularly, the most interesting thing was the possible existence of damage from the MLD method (c.f Fig. 5, 6). We already reported that a stable compound of B and Si is formed on the Si surface after MLD doping and its subsequent annealing, it is SiB$_6$ (boron silicide) [6], it is electrically non activated, it is several hundred Å thickness. The SiB$_6$ layer was to be removed by thermal oxidation (600°C, Dry O$_2$ ambient). However, possibly the thin Si$_x$B$_y$ (a part of transient region : SiB$_6$ - Si$_x$B$_y$ - Si) layer might remained at the upper most of the Si surface, which is not detected by SIMS signal (c.f Fig. 4). This thin Si$_x$B$_y$ layer is assumed to have a high density of boron, over the solid solubility but below the percent order, thus it might play the role of damage, and it is not affected by the annealing, because it is not a restorable crystalline defect but a stable compound. Stronger oxidation can remove the thin Si$_x$B$_y$ layer completely, but it may lead to boron segregation from the p$^+$ layer into a new growth of SiO$_2$, thus causing a decrease of the p$^+$ layer surface concentration. Optimal conditions for the removal process are to be explored during further study of this damage like phenomenon with the MLD method.

BF$_2$ I/I-PINs shows sufficiently tolerable photo sensitivity in terms of the optimal point of the fabrication process combination. It also suggests the possibility of achieving higher photo sensitivity, if it can survive damage restoration through RTA (Rapid Thermal Annealing) e.g and other annealing techniques [2] without a deepening of x$_j$.

By the way, the spectral responsivity might become a good analytical tool for the damage of shallow junction, and be useful in the field of ULSI process development instead of other expensive tools.

V. CONCLUSION

PIN photodiodes in which a p$^+$ layer is formed by MLD, is an inexpensive way to provide good performance for short-wavelength photo sensitivity. Because it uses furnace annealing and not RTA and it is not another dopant but a B, it is stable and trustworthy in terms of manufacturing. Accompany with the damage like phenomenon, MLD-PINs could achieve the highest performances of scintillation counting within this kind of current Si PIN photodiodes.

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