

Low Temperature Dopant Activation

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Abstract— A major area of research for integrated electronic systems is the development of systems on glass or plastic to optimize the performance/cost tradeoff. These new substrate materials impose significant constraints on electronic device fabrication, including limitations on chemical and thermal processes. Processes that do not use high temperatures have the increased flexibility needed to be used on new substrate materials. Amorphous silicon thin-film transistors (TFTs) have been fabricated at temperatures below 300°C, where in-situ doped layers are deposited to form the electrode regions. Unfortunately, the electrical activation and carrier mobility in these devices is exceedingly low. The conventional method of adding impurities is ion implantation. Interstitial impurities cannot contribute to conductivity, therefore electrical activation is critical for device operation. When a substrate is implanted with ions, the ions will break up the ordered crystal lattice and induce damage in the substrate. Annealing is a thermal process that serves two purposes, to recrystallize the substrate, and electrically activate dopant ions. While dopant activation at $T < 300^\circ\text{C}$ is not possible, anneals done at temperatures below 650°C can be quite effective. The goal of this project is to investigate methods of activating dopants without using the high temperature processes of conventional CMOS. A designed experiment is setup to investigate annealing behavior at low temperatures ($T \leq 650^\circ\text{C}$). Temperatures centered on 600°C are the focus of this design. Additional factors are investigated including annealing time, ion species, annealing technique (furnace or rapid thermal processing), and the use of pre-amorphization implants.

Index Terms—Ions, dopant, low temperature

I. INTRODUCTION

LOW temperature processing is important to integrated circuit fabrication for a variety of reasons. It provides process flexibility, as thermal processing can interfere with films or structures that compose the device to be fabricated. Several emerging technologies require a reduced thermal budget, including thin film transistors (TFT) and many other products. TFTs are devices built on a transparent substrate, such as glass, for use in display applications. While glass is excellent for optical applications, it has an adherent flaw, the melting temperature is significantly lower than the temperatures routinely used in transistor fabrication. Due to this thermal constraint, new methods are being investigated in

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order to realize transistors without high temperature processing.

II. THEORY

A. Problems with high temperatures

Many of the current process techniques used to fabricate today's complex integrated circuits (ICs) utilize high temperature thermal steps to achieve top grade transistors. For the purposes of this paper, high temperature is defined to be above 900°C, while low temperature is 600°C. The major processes that use high temperatures for transistor fabrication are dopant activation annealing and thermal gate oxide growth. Both of these steps are critical to the successful fabrication of CMOS devices. This paper examines the process of dopant activation annealing in detail.

B. Ion Implantation

A transistor is a three terminal device. The source, the drain, and the gate all affect the electrical characteristics of the device. In order to form the source and drain regions, ions must be added to selectively change the conductive properties in those regions. The primary method of introducing impurities into silicon is ion implantation. Implanting ions works by creating high-energy plasma from gas containing the ion desired for implantation, creating a collimated beam of extracted radicals from the plasma, and accelerating the ions through high voltages into the target. Typically, energies for such a process range from 20-200 KeV, depending on the ion species and type of implant desired. By tailoring the energies, ions can be implanted to a variety of depths and ranges, giving concentrated or deep profiles, depending on the desired application.

C. Dopant Activation

Acceptor or donor ions are implanted into the silicon for the purpose of changing its conductance. Only free electrons or holes contribute to conduction, and intrinsic (without any impurities) silicon is an insulator. It is only when impurities are added to the silicon does it conduct. Acceptor ions are those that accept free electrons and add a positive charge carrier, a hole, to the system. Donor ions are those that give up electrons. When the electron is given up, it can move freely above, also contributing to the overall conduction. However, for either acceptors or donors to contribute a hole or an electron, they must first replace silicon in the crystal lattice. This process is known as substitutional doping, or activation. Only some atoms can be used for this purpose. Acceptor

atoms are boron and indium, while donor atoms are phosphorus, arsenic, and antimony. This experiment focuses on boron and phosphorus due to availability.

D. Diffusion

Several conditions must be met for the dopant atoms to replace silicon in the crystal lattice, first, they must have enough energy to displace the silicon, plus enough energy to move about in the lattice until they find a suitable site. Typically a high temperature anneal is performed to give the ions enough energy to diffuse through the crystal lattice until they encounter a silicon atom. However, at temperatures below 800°C, diffusion does not take place on a suitable scale to be useful. Equation 1 shows the temperature dependence of diffusion.

$$D = D_0 e^{\frac{-E_a}{kT}} \quad (1)$$

The diffusion coefficient follows an exponential relationship with temperature, therefore, as temperature decreases, the amount of diffusion taking place decreases rapidly. At 600°C, the diffusion that takes place is almost zero and can be completely neglected. In order to improve the amount of dopant activation without increasing the temperature, the silicon must be amorphous. If the silicon is not crystalline when the anneal occurs, the thermal energy of the anneal will allow the silicon to rebuild the lattice. This recrystallization occurs at much lower temperatures than diffusion, typically beginning at 500°C. During the recrystallization process, if a dopant ion enters the lattice instead of a silicon atom, the dopant becomes electrically active, but requires less thermal energy. Amorphization is achieved by the ion implant process, since the ions have a great deal of energy as they enter the silicon wafer, they knock silicon atoms out of the lattice, making part or all of the implanted layer amorphous. Since different types of dopant all have different atomic mass, they amorphize different amounts. Heavier atoms amorphize the surface much more than light atoms. Therefore, the amount of amorphization is heavily dependent on the species of ions used for the implantation. The danger of amorphization is that if the anneal process does not completely repair the damage, the silicon layer will still be amorphous, and amorphous silicon has different carrier transport properties than crystalline silicon. The major difference is that the amorphous silicon will be much more resistive due to the lack of order in the structure, and this defeats the entire point of implanting ions in the first place.

III. EXPERIMENTAL DESIGN

A. Phosphorus Experiment

The first experiment examines the effect of the anneal on phosphorus activation. Fig. 1 shows the full experimental design. Many factors can effect the amount of dopant activation, however for this experiment, only the anneal conditions were varied. The implant dose was set at

$4 \times 10^{15} \text{ cm}^{-2}$ and implanted at an energy of 95 KeV. The energy was chosen to provide the peak of the ion profile at the surface of the wafer, given a screening oxide of 1000 Å. The screening oxide is necessary to ensure that the ions do not channel deep into the wafer by passing through the spaces in the crystal lattice. Three different temperature settings were used in the anneal process, 550°C, 600°C, and 650°C. These points were chosen because they should all allow the silicon to recrystallize, but not cause a glass substrate to melt. Two types of anneals were examined, a rapid thermal process (RTP) and a standard furnace tube anneal. By investigating both types, it can be determined whether a slower anneal has more of an effect on the activation process than the rapid thermal process. RTP annealing is standard for IC fabrication, however, it was believed that a longer furnace anneal might have a greater amount of activation, due to the longer times in the process. When examining the anneal time, several times were chosen for both types of processes. For RTP annealing, the anneal times were ten and sixty seconds. Ten seconds was the quickest the process could be done while still maintaining repeatability in the thermal profile. The furnace times were thirty minutes and one hour. Previous data suggests that one hour in the furnace should cause as much activation as possible for the given temperature. A thirty minute anneal is at the limit of the tool for repeatability and temperature stability. In addition, it was useless to do a furnace anneal for shorter than thirty minutes, since the process was designed for long, high temperature processing.

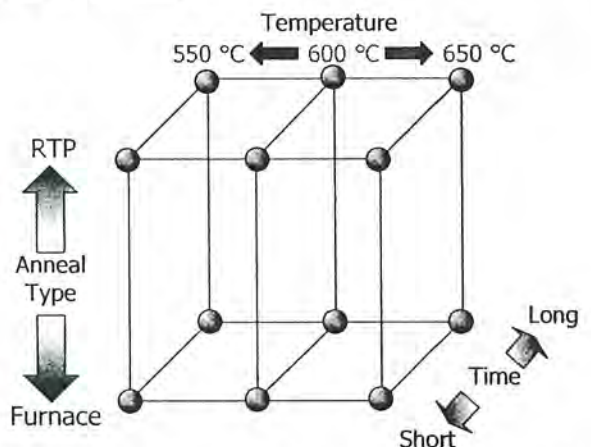


Fig. 1. Phosphorus experimental design. Anneal conditions vary for a set dose of phosphorus.

B. Boron Experiment

The experiment to investigate boron ion activation was performed after the phosphorus experiment, therefore, knowledge of the results helped dictate the experimental design. A greater investigation of how the implant dose affects the amount of activation was required for this experiment. A range of doses was used, going from 5×10^{12} to $8 \times 10^{15} \text{ cm}^{-2}$ to capture the full range of typical implanted doses. Six doses were done for boron. The implant species

was also varied, since there is a chose of molecules to implant with the boron trifluoride gas used to generate the plasma. Fig. 2 shows the mass spectrum for this gas. The main two species used for boron implants are B^{11} and BF_2 . BF_2 is used because it is a large molecule and thus can provide a greater degree of amorphization. Boron is very light and does not provide as much damage as its counterpart, phosphorus, which has an atomic mass of 31 amu. The implantation energies for these species changed to provide a similar profile to the phosphorus experiment, with the maximum amount of dopant concentration at the surface of the silicon layer. To provide the same profile with the same amount of screening oxide, the energies were set to 34 KeV for the B^{11} and 155 KeV for the BF_2 . The energy for the BF_2 is much greater because the energy must be split by the three atoms that make up the molecule. Due to the low amount of amorphization of the B^{11} ion, several experiments were done with a pre-amorphization step by implanting F^+ ions into the silicon before the boron was implanted. This process was limited to high doses because the application of low dose implants are threshold adjust implants in the channel region of the transistors. This region is critical for the device characteristics and should not be amorphized.

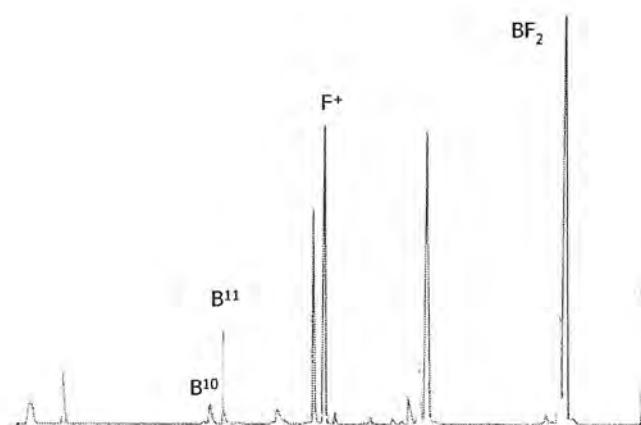


Fig. 2. Boron Mass Spectrum, principle peaks used in the experiment are highlighted.

The anneal conditions for the boron activation study were held to a temperature of 600°C while only the time was varied between 60 and 120 seconds. Only RTP anneals were performed on the boron study to limit the number of runs to a sizeable amount. The increase in anneal time for this experiment was done because initial data suggested that a ten second anneal was inadequate to remove silicon damage from the pre-amorphization. See table 1 for the full gamut of experiments run for boron.

TABLE 1

B^{11} Experiment

Type	Pre-amorph	implant Dose	Temp	time
RTP		5.00E+12	600	60
RTP		5.00E+12	600	120
RTP		1.00E+13	600	60
RTP		1.00E+13	600	120
RTP		1.00E+14	600	60
RTP		1.00E+14	600	120
RTP	3.00E+15	1.00E+14	600	60
RTP	3.00E+15	1.00E+14	600	120
RTP	3.00E+15	1.00E+15	600	60
RTP	3.00E+15	1.00E+15	600	120
RTP	3.00E+15	4.00E+15	600	60
RTP	3.00E+15	4.00E+15	600	120
RTP	3.00E+15	8.00E+15	600	60
RTP	3.00E+15	8.00E+15	600	120

BF_2 Experiment

Type		implant Dose	Temp	time
RTP		1.00E+15	600	60
RTP		1.00E+15	600	120
RTP		4.00E+15	600	60
RTP		4.00E+15	600	120
RTP		8.00E+15	600	60
RTP		8.00E+15	600	120

IV. MODELING

In order to accurately predict the amount of dose that activates upon annealing, a model was required. By using Silvaco Suprem simulation software, implants were simulated over a range of doses and the resulting sheet resistance of the structure was found. The simulated data plots can be seen in figs. 3 and 4, for phosphorus and boron respectively. This data allowed a model equation to be generated that could predict the electrically active dose for a given sheet resistance value.

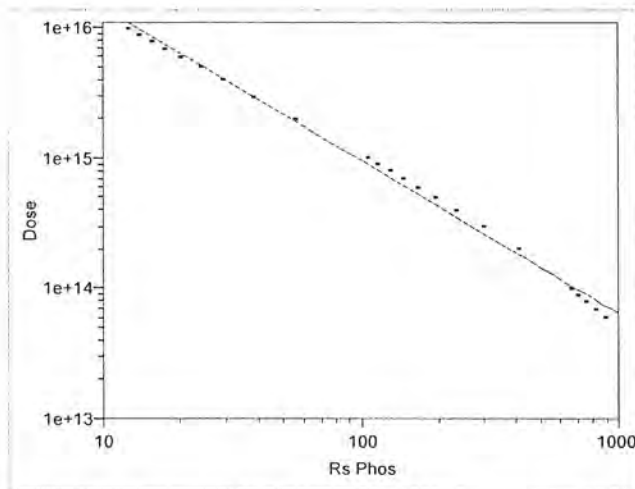


Fig. 3. Phosphorus Simulated data for Sheet resistance versus implant dose.

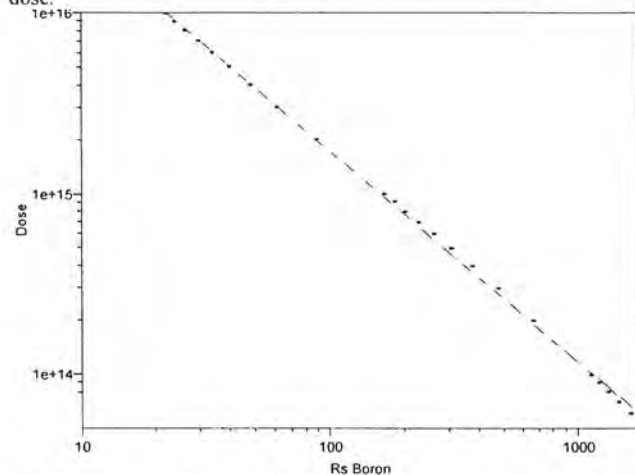


Fig. 4. Boron Simulated data for Sheet resistance versus implant dose.

In order to model boron implantation, two models were required, since the range of doses was much larger. The model equations are shown in (2), (3), and (4), for phosphorus, low dose boron, and high dose boron respectively.

$$\ln(\text{Dose}) = 39.924 - 1.174 \ln(R_s) \quad (2)$$

$$\ln(\text{Dose}) = 43.048 - 1.539 \ln(R_s) \quad (3)$$

$$\ln(\text{Dose}) = 40.486 - 1.169 \ln(R_s) \quad (4)$$

The low dose boron model is valid for doses lower than 5×10^{13} while the high dose model is valid for greater doses. In all of the equations, a small change in sheet resistance can give a large change in predicted dose value. This necessitates a highly accurate sheet resistance measurement.

The metric used to compare the success of various anneal settings is the percentage of active dopant. This number is calculated by using the model equations to predict the active dose from a sheet resistance measurement and comparing it with the amount of dose implanted. This means that if there was 50% activation, half of the ions implanted into the silicon became electrically active during the anneal.

V. RESULTS

A. Phosphorus Experiment

The phosphorus experimental results are summarized in fig.5. The major result from the phosphorus experiment was that RTP activated 10% more dopant, overall, than the furnace anneals. There could be several reasons for this. The thermal profile the furnace tube is different from the profile for the RTP system. The ramping to the steady-state temperature took 5 seconds for the rapid thermal system, however the ramp step for the furnace took about 20 minutes. This means, that even though the samples saw significantly longer times at elevated temperatures, the activation was not improved. One of the dangers of the furnace anneal was spiking above the set point. This is a problem because once new materials are incorporated into this process, a thermal spike that is significantly above the allowed temperature could ruin the material. In attempts to avoid this, the furnace recipe was set such that the time it took to reach the final temperature was very long. This might have caused slightly less activation than otherwise, however it is still preferred, since the thermal spiking could cause much more activation. Variations in anneal temperature did not have a marked effect on the percent activation. Anneal time alone does not have a major impact on the percent activation. The one data point of note is 550°C RTP anneal for ten seconds. This point is notably lower than all the other points. It is determined from this that while neither temperature or time has a major impact, the combination of them both at the lowest setting does impact the percent activation, giving about 50% less dopant activation. The data here was used to predict results for the boron experiment and eliminate needless runs, such as further furnace processing.

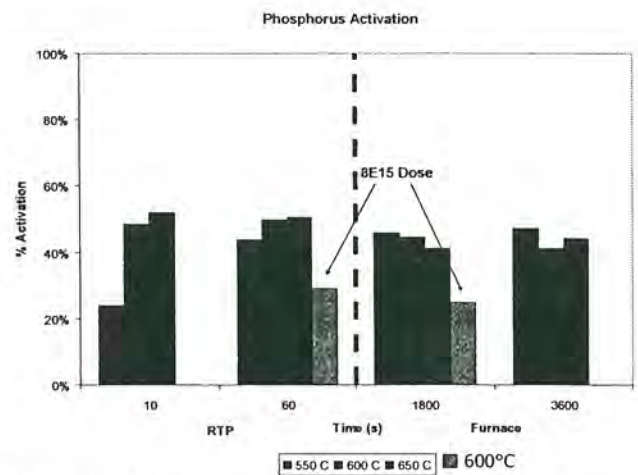


Fig. 5. Results from the phosphorus experiment for three anneal temperatures. Samples with RTP anneals are shown on the left, while those done by furnace annealing are shown on the right.

Several data points were taken at a higher dose (8×10^{15}). These points activated less dopant nearly 50%, meaning that there is a saturation point for these anneals conditions where only a fixed amount of dopant can activate, adding more does not improve the activation.

B. Boron Experiment

The data for the boron experiment cannot be condensed into one chart; refer to figs. 6, 7, 8, 9 and 10 for the full set of data. Since the phosphorus experiment determined that the anneal temperature did not have a significant effect on the activation levels, the boron implant anneals were investigated by exploring how the amount of dopant implanted affected the amount that would electrically activate. The results of the

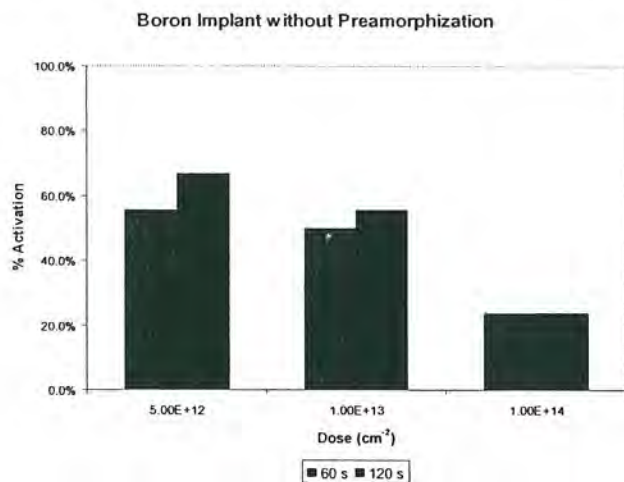


Fig. 6. Boron results for no pre-amorphization and both anneal times. Three doses were examined at this condition.

boron experiment show a decreasing linear trend in the data, meaning that there is limits to the amount of dopant that can activate at these anneal conditions. The anneal time has a minimal effect on the dopant activation, and has a steady decrease in effect as the dose increases. As the silicon is implanted at higher doses, it also becomes more amorphous. Because more amorphization goes on, it is easier for the crystal structure to be rebuilt, since there is no initial order. This implies that the implant damage can be repaired faster, therefore longer times are not necessary and add no more activation. The pre-amorphization of the higher dose implants show that the saturation point can be increased with a fluorine implantation, however pre-amorphizing with the lower dose implants does not improve the activation by a similar amount. This can be explained by the fact that the boron itself can amorphize the surface, therefore at lower doses there is not enough amorphization done to the silicon to allow the dopants to electrically activate. The amount of damage done to the silicon directly relates to the amount of dopants that activate, as initially expected. Fig. 7 also shows an improvement in the sample that was annealed for 120 seconds that received a pre-amorphization. The sample that was annealed for only 60 seconds was similar to those without the pre-amorphization. This implies that there is potential for activation with amorphization, even at this lower dose, however, 60 seconds is not long enough to fully realize this activation.

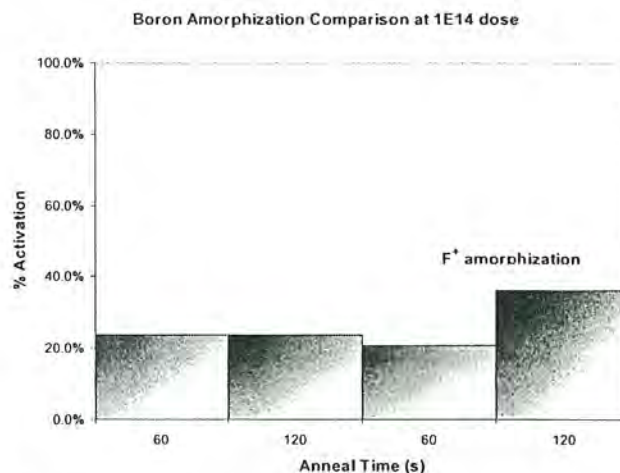


Fig. 7. Effect of pre-amorphization on activation and anneal time. The rightmost two bars are for samples with fluorine pre-amorphization while the left two did not receive any.

The high dose boron implantation with a pre-amorphization step all show much higher levels of dopant activation. Once again, a decreasing trend in the data is obvious. Therefore, even with a pre-amorphization, there is still only a certain amount of dopant ions that can become electrically active, without the aid of diffusion. Again, it can be seen that the anneal time plays a role in the activation, however as the amount of amorphization increases, the anneal time has less of an effect. With the pre-amorphization, the effect of the anneal time has an extended range, effecting almost all of the doses used.

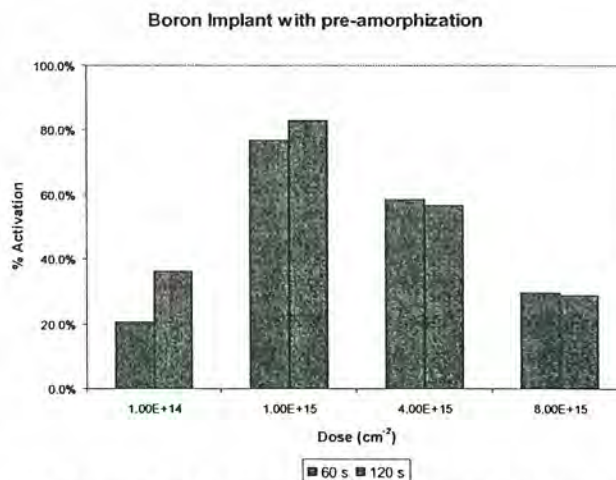


Fig. 8. Activation data for boron with pre-amorphization split by anneal time. A dose of 1E15 gives 80% activation.

The BF₂ implant study gave much lower levels of activation for all three doses used. This implies that the amount of amorphization of the BF₂ molecule is less than a pre-amorphization of just F⁺ alone. This is counter-intuitive, because there is more fluorine present in the BF₂ than in the single F⁺ for the pre-amorphization step. However, the fluorine ions from the BF₂ molecule do not necessarily travel the full distance into the silicon that the boron does. This

implies that the fluorine pre-amorphization amorphizes deeper into the silicon than the B¹¹ implant depth. Note that the BF₂ data retains the decreasing amount of activation as the dose is increased that was seen in the other boron studies.

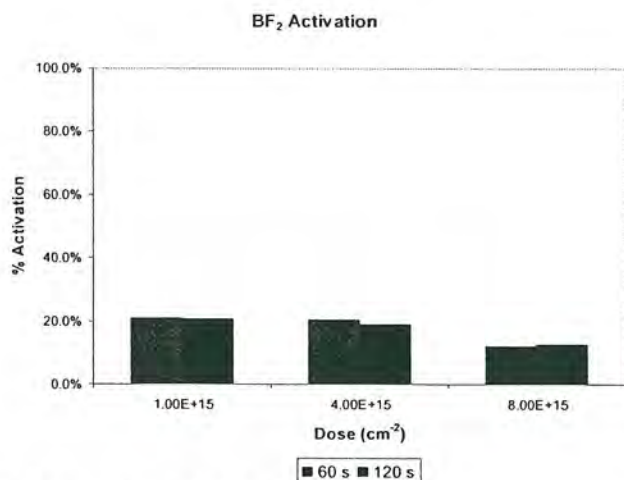


Fig 9. Activation data for BF₂ split by anneal time.

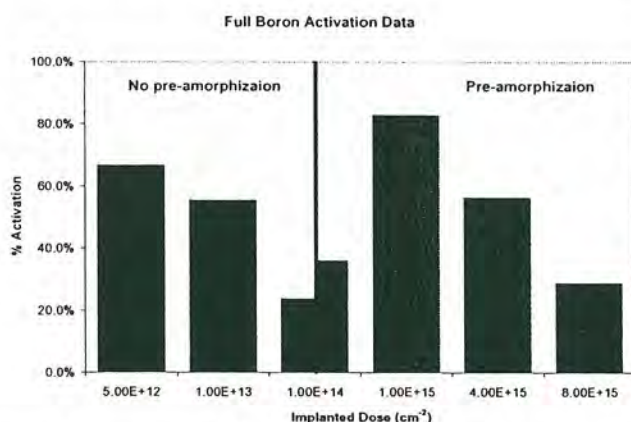


Fig. 10. Comparisons of all boron implants with 120 second anneal. The blue bars represent the implants without fluorine implants and the red bars show the implants done with a pre-amorphization.

VI. CONCLUSION

Various improvements have been made to the methods of dopant annealing at low temperatures. From this experiment, it can be seen that rapid thermal processing provides a higher degree of dopant activation than traditional furnace processing at lower temperatures. The crystallinity of the silicon and amount of damage done to the surface during the implantation is a key factor to promote low temperature activation. The duration of the anneal can have an effect on the amount of activation that occurs; this effect is determined by the amorphous state of the silicon.

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