공학연구논문집 제27권 제1호 pp. 183~195, 울산대학교
Journal of Engineering Research Vol. 27, No. 1, pp. 183~195, 1996.
University of Ulsan.

Si Surface Modification After Self-implantation And Subsequent Hydrogenation

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<Abstract>

Si self-ion implantation was performed to study changes of the electrical properties of the n-type and the p-type Si. The implanted n-type samples were exposed to the hydrogen plasma during different exposure times. The electrical properties of the Schottky diode structures were measured and compared before and after implantation with and without hydrogen plasma exposure. While the Schottky barrier height on n-Si changes after implantation, constant barrier height has been observed for p-Si. Deep level transient spectroscopy (DLTS) measurements reveal that four deep-level defects are created in the n-Si after implantation and that their concentrations change with increasing hydrogen plasma exposure time. It has been confirmed that vacancy-related defects are passivated by hydrogen earlier than other defects.

Si^+이온 주입과 수소 플라즈마 처리에 따른 단결정 Si표면의 특성변화

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<요 약>

실리콘 이온을 주입하여 n형과 p형 실리콘의 전기적 성질의 변화를 연구하였다. 주입된 n형 실리콘을 처리시간을 변화시키며 수소 플라즈마로 처리하여 주입전후의 실리콘의 전기적 측정 결과를 수소 플라즈마 처리 여부에 따라 비교 분석하였다. Schottky 다이오드

의 전류-전압측정 결과, 이온주입이 p형과 n형 실리콘의 성질을 다른 방법으로 변화시키는 것으로 나타났다. 이온주입후 형성된 네가지 deep level들과 수소 플라즈마 처리시간의 증가에 따른 그 결함들의 농도 변화를 DLTS로 측정하였다. 공공과 관련된 결함들이 다른 결함들 보다 먼저 수소에 의해 비활성화되는 것이 확인되었다.

1. Introduction

Semiconductors are exposed to the environments, which may affect properties of the materials, during device fabrication processes. Many processes induce deep level defects which may deteriorate the performance of the final devices in most cases. Deep levels act as efficient recombination centers and thus reduce minority carrier lifetime significantly[1].

Ion implantation is a commonly used method to introduce impurities into semiconductors. Implantation enables us to control precise amounts of the implanted dopants and the depth of the peak concentration. However, since ions are accelerated with medium to high energy (several keV to several MeV), implantation inevitably accompanies lattice damage and annealing at elevated temperatures is required to remove the damage. Ion implantation is known to introduce vacancy-related defects and impurity-related defects[2]. High dose implantation-induced defects include stacking faults and dislocation loops[1]. Annealing kinetics of defects are very complex and closely related to the presence of impurities such as carbon, oxygen, and dopants[3].

Hydrogen is known to passivate almost every kind of defect. In spite of the limited practical use due to its thermal instability, much concern has been paid to hydrogen because of the possibility of hydrogen penetration in almost every semiconductor process step and its capability to alter severely the physical properties of the semiconductor. As well as hydrogen passivates defects, hydrogen itself creates defects in otherwise perfect crystals[4]. Hydrogen interacts with Si lattice in a very complex way. It has been shown that hydrogen plasma exposure may induce latent defects with high concentrations near the Si surface[5]. Hydrogen is implanted at low ion energy to passivate a-Si for solar-cell applications[6]. It is also shown that, after hydrogen passivation, the damage is annealed at a temperature (500-600℃) which is much lower than the anneal temperature of as-implanted defects[7].

For this study, Si self-ion was implanted to investigate the changes of properties of the Si near-surface region. Silicon ion was chosen to avoid any impurity-related effects. The implanted samples were exposed to the hydrogen plasma during various exposure time. Electrical measurements were performed and the properties of the implanted samples were compared before and after hydrogen plasma exposure.

2. Experimentals

Both n-type and p-type (100) Si wafers were used for this study. The n-type Si was doped with phosphorous to a concentration of $1.3\text{x}10^{15}$ cm^{-3} and the p-type Si was doped with boron to a concentration of $2\text{x}10^{15}$ cm^{-3}. Si ions were implanted into p-type and n-type Si wafers with an ion energy of 20 keV. A commercial ion implanter, Model Varian 350D, was used to implant Si self-ions. The implantation ion doses for the n-type samples were 10^{12}, 10^{13}, 10^{14} cm^{-2}, and for the p-type samples 10^{13} and 10^{15} cm^{-2}.

For hydrogenation study, the implanted samples were exposed to hydrogen plasma in the ECR chamber for varying exposure times without additional heating. As shown in Figure 1, the ECR system is a horizontal type in which the sample is placed away from the plasma region to avoid surface damage due to direct immersion of the samples in the plasma. The ECR ion source, from Applied Science and Technology, Inc., can be supplied with microwave power of 200-1000 watts. The system has two water-cooled electromagnets, a 2.45 GHz tunable waveguide, a mechanical pump, and a turbomolecular pump. The residual gas analyzer is equipped as a monitoring system for the various gases. The ECR operating conditions are summarized in Table 1.

The Schottky diode structure was used to study the defects after ion implantation and hydrogenation with I-V and DLTS measurements. Au was thermally evaporated through a shadow mask onto the front surface of the n-type samples for 1 mm^2 area Schottky contacts. For 1 mm^2 area p-type Schottky contacts, Ti evaporation followed by Al evaporation was used to protect Ti against oxidation. Ohmic contacts were made by evaporating Ti/Al and Al onto the back surface of the n-type and the p-type substrates, respectively. Evaporation for both contacts was done at a base pressure of about $1\text{x}10^{-7}$ Torr. A Hewlett-Packard 4145B Semiconductor Parameter Analyzer and a BioRad DL 4600 system were used for the I-V characterization and DLTS measurements, respectively. Annealing was done in a conventional furnace under N_2 ambient before metal evaporation to identify the defects.

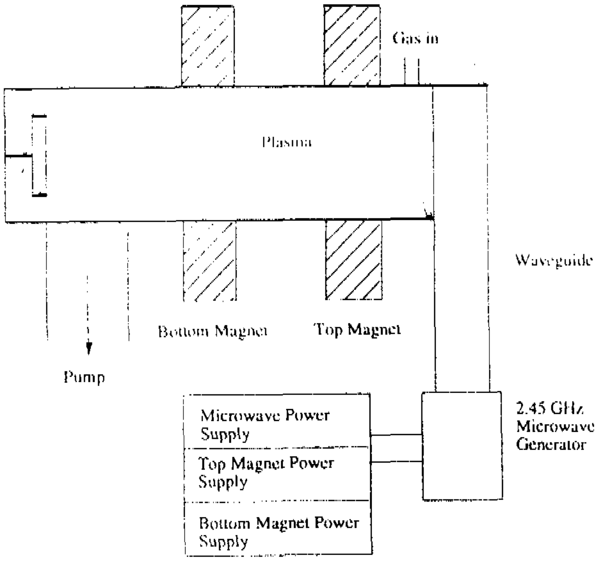

Figure 1. A schematic of the ECR system.

Table 1. The ECR operating conditions for hydrogen plasma exposure.

Base operating pressure	1x10^{-6} Torr
Gas flow rate	2.8 sccm
Operating pressure	0.15 mTorr
Power	600 W
Exposure time	10, 15, 30, 120 minutes
Distance between top and bottom magnets	12.5 inches

3. Results and Discussion

The n-type and the p-type Schottky diode samples showed different I-V characteristics after implantation. Figures 2 and 3 show the I-V curves of the n-type and the p-type Schottky diodes after Si self-implantation with different implantation doses, respectively. As shown in Figure 2, the reverse saturation current of the n-type sample does not change significantly after implantation at a dose of 10^{12} cm^{-2}, but increases as the implantation dose increases beyond 10^{12} cm^{-2} to 10^{14} cm^{-2}.

Electrical measurements on Schottky diode structure measure the properties around the depletion region (up to several microns deep). Therefore, these are near-surface-sensitive measurements, and are not deep-bulk-sensitive. The modification of the barrier height and the exponential dependence of current on the effective barrier height make the Schottky structure very sensitive to the electrically active defects and contaminants near the interface of the diode.

Si self-implantation into n-type samples reduces surface barrier height, with monotonic dependence on doses (Figure 2). As a result of barrier height reduction, the reverse saturation current of the n-type Schottky diodes increases with increasing dose from 10^{12} cm^{-2} to 10^{14} cm^{-2}. This well-established barrier height reduction of n-type Schottky diodes results from ion-bombardment-induced donor-like defects that modify the depletion region profile[8]. The reverse current of the implanted sample at a dose of 1×10^{14} cm^{-2} increases by four orders of magnitude compared to the control sample, which means that the surface region of the Si sample is severely damaged by the implantation.

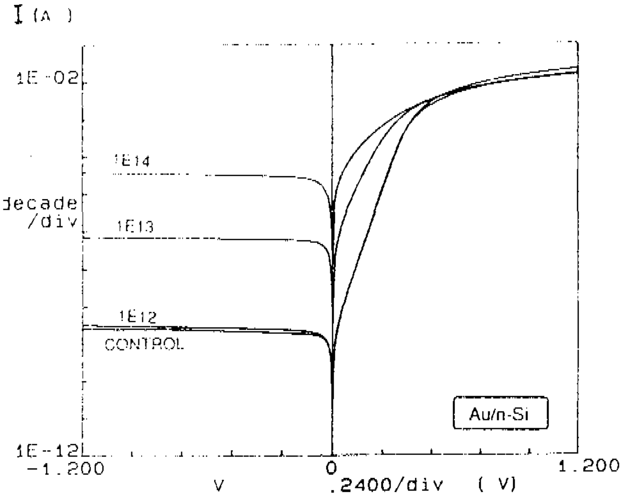

Figure 2. I-V curves of the n-type Schottky diodes as a function of implantation doses.

The reverse current of the p-type Schottky diodes did not change after implantation as shown in Figure 3. Even though the implantation dose is changed from 1×10^{13} cm^{-2} to 1×10^{15} cm^{-2}, the reverse current remains the same as that of the sample before implantation. To check if this is caused by Fermi level pinning, ohmic contact was made with the p-type Si by evaporating Al on the front surface and the back surface. The I-V curves of these ohmic contacts are shown before and after Si self-ion in Figure 4. For comparison, Ar ion was implanted at a dose of 1×10^{13} cm^{-2} with an ion energy of 20 keV. In Figure 4, Al metallization on the front and back surfaces of argon implanted p-type sample showed ohmic I-V curves, as expected. However, Si self-implanted samples with ohmic contacts still show the same I-V characteristics as that of the Schottky diode with Ti metal layer on the front surface. Figures 3 and 4 show that, after Si self-implantation, the barrier height does not change regardless of the kind of metal evaporated on the front surface. Therefore, we concluded that Fermi-level pinning occurred after Si self-implantation but not after argon implantation.

It is known that the barrier height of the p-type Schottky diode increases due to the introduction of donor-like defects after ion implantation. However, our experiment showed that Fermi level pinning occurred in the p-Si after Si self-implantation at a dose of 1x10^{13} cm^{-2}. This is not an expected result since a low dose of implantation, 1x10^{13} cm^{-2}, leads to the Fermi level pinning. It is not known why Fermi level pinning occurs after Si self-implantation at a low dose below the amorphization threshold dose (about 1x10^{15} cm^{-2}). The Fermi-level pinning did not occur after argon ion implantation at the same dose, which eliminates the possibility of the effect due to contamination during implantation.

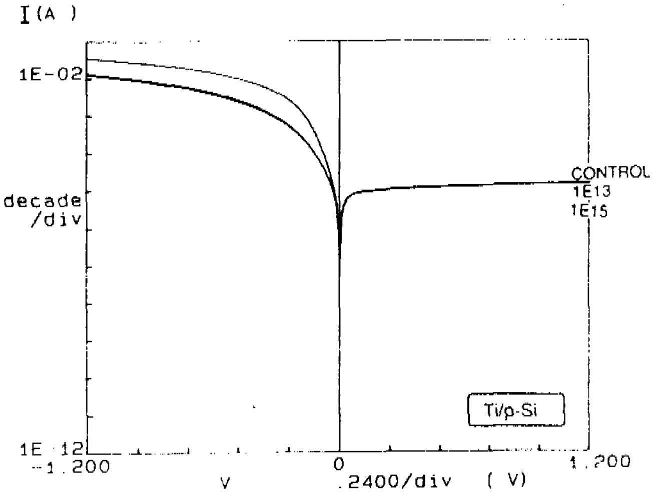

Figure 3. I-V curves of the p-type Schottky diodes as a function of implantation doses.

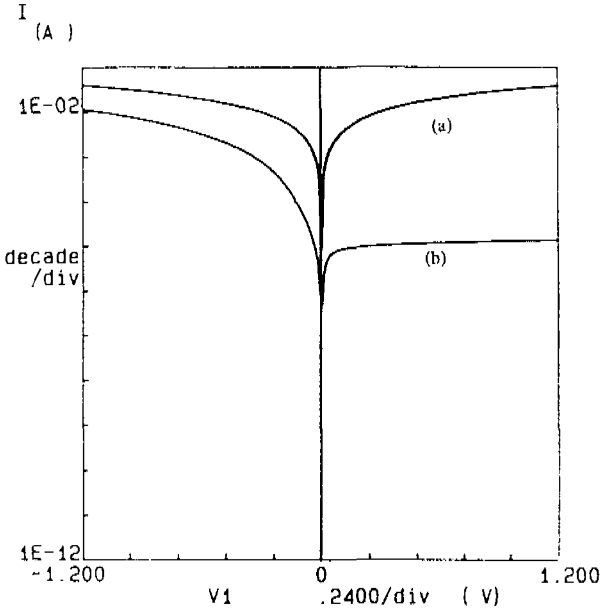

Figure 4. I-V curves of the p-type samples with ohmic contacts on the front and back side after (a) argon ion and (b) Si self-implantation at a dose of $1x10^{13}$ cm^{-2}.

Interstitial Si is known to be unstable, migrating until trapped at impurities even at temperature as low as 4.2K. From electron paramagnetic resonance (EPR) measurements, Watkins has established that the trapped interstitial Si trades places with boron which is an impurity in p-Si, and, as a result, boron takes the interstitial site [9]. The interstitial boron atom has a deep level at 0.45 eV below the conduction band[10]. It is not apparent that these unstable interstitial Si atoms may result in Fermi level pinning of the p-Si samples shown in Figure 3. It is also known that, in n-type Si, the interstitial Si atom is much less mobile.

From TRIM code simulation for implantation conditions used in this study, the projected range of 20 keV Si^+ ion is about 330 Å and the maximum damage occurs at a depth of 200 Å. DLTS measurement was done with the n-type Schottky diodes after self-ion implantation at a dose of $1x10^{13}$ cm^{-2}. Figure 5 shows the DLTS spectrum of the n-type sample measured at a reverse bias of -3 V after implantation at 20 keV. Four dominant electron traps were detected, of which energy levels were measured as 0.29 eV, 0.31 eV, 0.39 eV, and 0.41 eV, respectively.

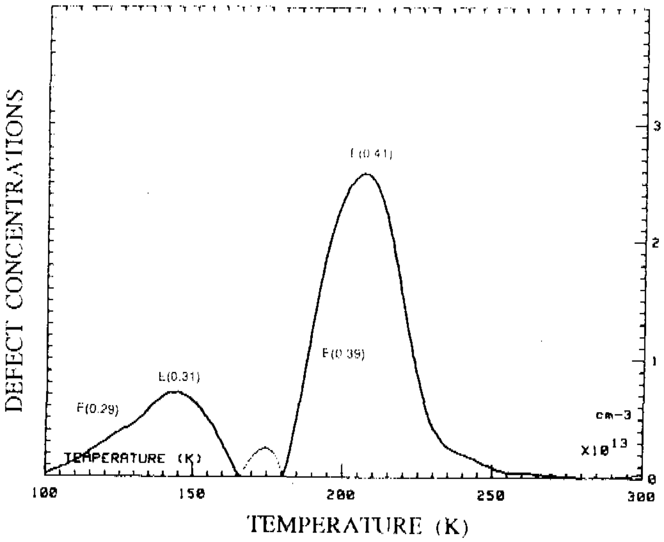

Figure 5. DLTS spectrum of the n-Si Schottky diodes after implantation of 20 keV Si$^+$ at a dose of 1x10^{13} cm^{-2}.

Annealing was done to identify the vacancy-related defects. After anneal at 150℃, the concentrations of E(0.41) and E(0.39) decreased slightly. However, E(0.41) was annealed out at 350℃ and E(0.39) decreased by about one order of magnitude at the same temperature. It is known that ion bombardment with high energy produces lattice disorder, including single vacancy or higher order vacancies. Although the single vacancy is annealed out at about 100K, vacancies form complexes with other impurities as can be found in most ion implanted samples[3]. Divacancy is known to introduce three energy levels in the forbidden bandgap, that is H(0.21), E(0.41), and E(0.23), and annealed out at 300℃ [2]. The phosphorous-vacancy complex has the energy level of 0.44 eV from the conduction band, and is annealed out at 150℃[2]. The divacancy peak overlaps with the phosphorous-vacancy peak, because of their close location in the bandgap. The energy level and the annealing kinetics of E(0.41) are consistent with the nature of the phosphorous-vacancy (P-V) and/or the divacancy (V-V) (-/0 charge state) complexes and E(0.41) is a vacancy-related trap as a combination of divacancy and phosphorous-vacancy complexes. Other peaks are thought to be due to defects not related to the vacancy as evidenced from their energy levels and annealing kinetics.

After implantation, the n-type samples were exposed to the hydrogen plasma in an ECR chamber. Hydrogenation for 10 minutes was not effective in reducing the defect concentration at ECR operating conditions used for this study; none of the defects were passivated and the concentration of E(0.31), in fact, increased by a factor of 2. After 15 minute hydrogenation, the defect concentrations began to decrease. Observation of the defect concentration after hydrogen plasma exposure shows that there is a competition between increase in defect concentration and hydrogen passivation. The increase of the defect concentration may be due to the temperature rise, though not high, during the plasma exposure. It has been estimated that sample temperature is maintained below 250℃ after 30 minute hydrogen plasma exposure and does not increase for longer exposure.

Figure 6 shows the I-V characteristics of the n-type Schottky diodes self-ion implanted at a dose of $1x10^{13}$ cm^{-2} before and after hydrogenation. The reverse saturation current increases by about three orders of magnitude after implantation and decreases gradually as hydrogen plasma exposure time increases. As plasma exposure time increases from 30 minutes to 2 hours, the reverse current decreases further. However, even after 2 hour hydrogenation, the reverse current is still higher than that of the control sample.

The reduced barrier height on n-Si due to implantation damage increased after hydrogen plasma exposure (Figure 6). It is interesting to note that all implantation-induced deep level defects were passivated after a 30 minute hydrogen plasma exposure under the bias conditions for the DLTS measurement, but the reverse current of the Schottky diode was still much higher than that of the control sample. Even after 2 hour plasma exposure, the reverse saturation current was not restored to that of the control sample, which means that the implant damage was not completely passivated by atomic hydrogen.

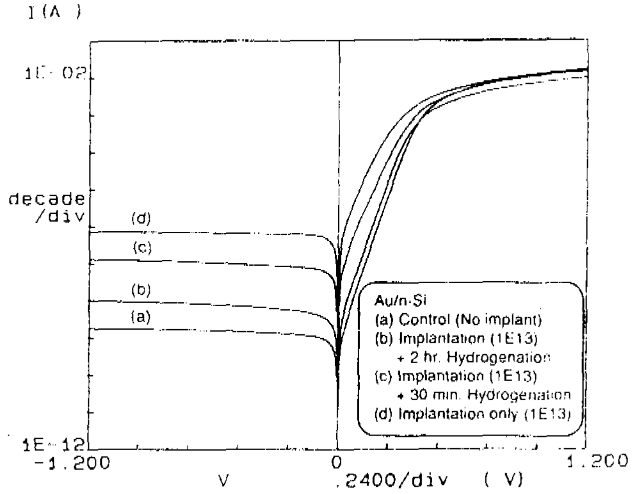

Figure 6. I-V curves of the n-type Schottky diodes after implantation and hydrogenation.

It is believed that, after dehydrogenation, the state of the hydrogenated defects will be different from the state before hydrogenation. We tried annealing studies with implanted and subsequently hydrogenated samples but did not get meaningful data. However, the original defects, e.g. E(0.41), did not appear after dehydrogenation.

The p-type samples did not show any noticeable change after implantation and hydrogenation (Figure 7). This is an expected result because Fermi level pinning has occurred after implantation. Any effects due to hydrogen plasma exposure, such as plasma irradiation on the surface and the change of the effective dopant concentration due to passivation, do not change the barrier height of the diode.

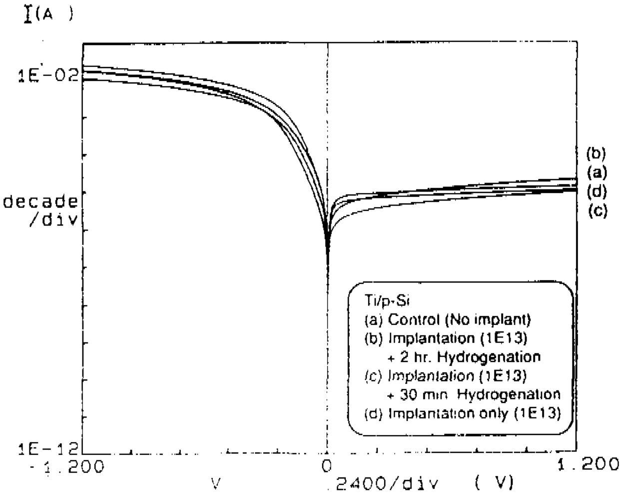

Figure 7. I-V curves of the p-type Schottky diodes after implantation and hydrogenation.

The n-type samples implanted with Si ions ($1x10^{13}$ cm^{-2}) were exposed to the ECR hydrogen plasma. Figure 8 shows the DLTS spectra before and after hydrogenation for 15 minutes. The peaks are slightly shifted after hydrogenation, which is probably due to the disappearance of the minority carrier trap. Plasma exposure for 15 minutes does not seem to passivate the defects. Since the plasma exposure was done without heating, it is likely that no enough hydrogen has diffused into the Si to passivate the defects.

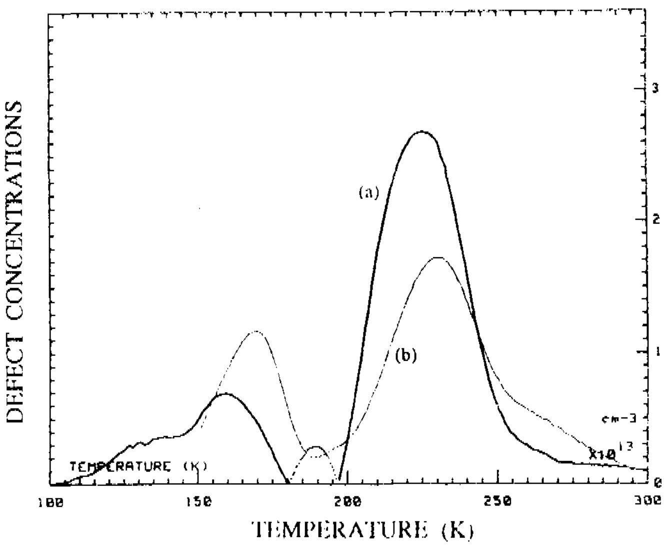

Figure 8. DLTS spectra of Si self-implanted n-Si samples at a dose of $1\times10^{13}cm^{-2}$(a)before and (b)after 15 min hydrogen plasma exposure.

Figure 9 shows the normalized defect concentrations of the implanted n-type samples after hydrogen plasma exposure for different exposure times. After 10 minute hydrogenation, the concentration of E(0.31) increased almost two times while other defects did not increase much. After 15 minute exposure, the concentration of E(0.31) do not change but other defects are decreased. No DLTS peak was observed after 30 minute exposure, indicating that active defects are present below our DLTS system detection limit if any. For our DLTS system, the minimum detection limit of defect concentration is estimated as about 10^{-4} of the dopant concentration Since the concentrations of defects except vacancy-related defects, E(0.41), do not change even after 350℃ anneal, disappearance of defects is due to the passivation by hydrogenation. As shown in Figure 9, it is likely that hydrogen prefers the vacancy site and that vacancy-related defects are passivated earlier than other defects. Theoretical calculations have shown that hydrogen is attracted most to the vacancy-like defects and impurities, which agrees with our experimental results[11].

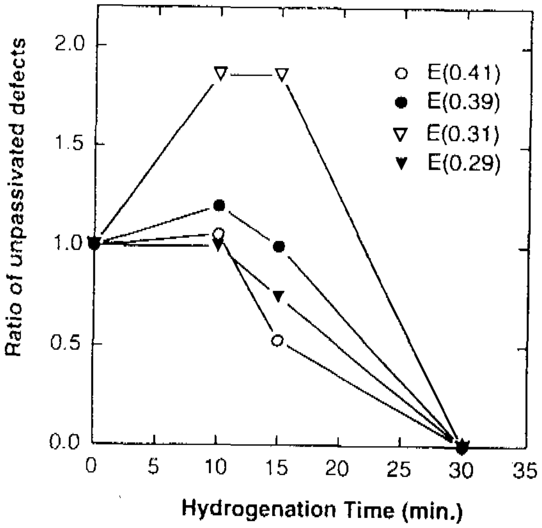

Figure 9. Normalized defect concentrations of Si implanted n-Si (1×10^{13} cm^{-2}) after hydrogen plasma exposure for different exposure times.

4. Conclusions

Silicon self-ion implantation decreases the barrier height of the n-Si Schottky diodes and induces four deep level defects in the n-Si. Hydrogen exposure restores the barrier height of n-Si which is reduced after implantation. However, even after two hour exposure, the barrier height is not completely restored. In the p-Si, Si implantation at a dose of 1×10^{13} cm^{-2} leads to Fermi-level pinning. Fermi-level pinning did not occur after argon ion implantation at the same dose. Hydrogenation study showed that hydrogen prefers the vacancy site and passivates preferentially vacancy-related defects. After a 30 minute exposure, no defects were detected.

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