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Hydrogenation and annealing studies on swift heavy ion (Au^{7+}) irradiated Pd/p-Si devices

S. P. PANDEY*, B. BHATTACHARYA[a], U.P. SINGH[b], K. ASOKAN[c]
Galgotia College of Engineering and Technology, Greater Noida (U.P). INDIA
[a]*Hindustan College of Science and Technology, Farah, Mathura, INDIA*
[b]*KIIT University, Bhubaneshwar, INDIA*
[c]*IUAC (Nuclear Science Centre), Aruna Asaf Ali Marg, New Delhi, INDIA*

Electronic properties of the Pd/p-Si devices have been studied from J-V and C-V characteristics as a function of irradiation fluence, hydrogenation and annealing temperatures to understand the phenomenon of degradation of Pd/p-Si devices when exposed with swift heavy ions, 100 MeV Au(7+). It has been found that the diode characteristics of the devices become poor and show an increased resistivity after irradiation. The irradiated devices were hydrogenated with an aim to repair the irradiation damage. Annealing of these devices was carried out at temperatures ranging from 100°C to 400°C. The I-R spectroscopic studies on the irradiated and subsequently annealed devices show the presence of vacancies and their complexes with impurities like hydrogen, carbon and oxygen. The results have been discussed in the realm of radiation induced compensating defects causing the carrier removal phenomenon to increase the resistivity of the devices on irradiation.

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1. Introduction

Swift heavy ion beams plays a vital role in the modification of the properties of semiconductors materials and its devices. Understanding the role of swift ion radiation induced defects and its complexes with impurities will result to the precise development of new generation technology of devices and solar cells [1-5]. It is well known that the ion irradiation into semiconductor causes structural damage, which in turn results in electrically active defect. Theses electrically active defect may complex with other impurity which changes the electrical parameters of semiconductor devices. Presence of swift heavy ion irradiated defect centers decrease the net ionized donor concentration [1] which results to the increase in series resistance [2]. Impurities like carbon, oxygen are also expected to influence the formation of defects during the swift heavy ion radiation.

The incorporation of atomic hydrogen into crystalline semiconductor causes significant change both in the electrical as well as optical properties of the materials [6,7]. Hydrogen in crystalline silicon semiconductor is significant because of its ability to passivate the electrically active dangling bonds [8,9]. To measure the hydrogen content and to study the profile across the hydrogenated Pd/p- Si devices, elastic recoil detection analysis (ERDA) measurements have been already performed with high energy heavy ions [10]. It has been established that the presence of ions at the depth of its range produces change of both physical and chemical properties of the materials.

Annealing of the irradiated silicon devices are carried out because of the radiation induced defects change their configurations after annealing. The large concentration of defects decrease the current density and recovery of it reflects the passivation of defects after annealing at different temperatures. The degradation in the electrical properties due to swift ions and its recovery with annealing temperatures was reported by Srivastava et al. [11]. Annealing generally causes the passivation of defects which cause the reduction in the number of defects and increases their separation. The defects may complex with impurities and act as trapping or recombination centers which may move with annealing temperatures. Carbon and oxygen are well known impurities in silicon which occupy interstitial position. Carbon can also occupy isolated substitutional sites [12]. Interstitial oxygen atom in silicon traps mobile vacancies to produce V-O complexes known as ‘A’ centers. These centers may also change their configuration i.e. V-O may change to VO_2 by trapping one more interstitial oxygen as $VO + O_i = VO_2$. The two VO centers may also combine to give rise to a VO_2 and release a vacancy $VO + VO = VO_2 + V$. These VO_2 centers can further trap interstitial oxygen to form VO_3 complexes [13].

In the present study, the electronic properties of high energy heavy ion irradiated Pd/p-Si devices are described. Electronic properties have been studied from J-V and C-V characteristics of the devices. The irradiated devices were hydrogenated and subsequently annealed with an aim to modify the radiation induced defects. The IR spectroscopic study on the irradiated and annealed Pd/p-Si device has been carried out for the investigation of the presence of di-vacancies and their complexes (with impurities like hydrogen, carbon and oxygen). The energy and the concentration of the radiation induced deep states have also been estimated from C-V characteristics.

2. Experimental

Pd/p-Si devices were fabricated by vacuum deposition of Palladium film of 200Å on various substrates. We have used Pd as a metal for Schottky contact in view of hydrogenating the devices. The p-Si substrates were <111> cut p/p+ wafer of 2-3 ohm-cm. The thickness of the epi-layer was 12-18μm. The wafers were given to a quick chemical etch in a solution of $HF:HNO_3:H_2O$. The wafers were, then, thoroughly rinsed in de-ionized water and dried in a clean chamber before the metal deposition. The palladium metal was deposited as dots of 0.5 mm diameter, by electron beam evaporation technique in vacuum chamber at $\sim 10^{-6}$ torr. These devices were characterized through J-V and C-V measurements. The I-R spectroscopic studies have been carried out using a Perkin-Elmer (820) spectrophotometer for the irradiated and also subsequently annealed devices. The J-V and C-V measurements were performed using Keithley SMU-236 and HP 4277 LCZ meter respectively prior to and also after the heavy ion irradiation and hydrogenation. The frequency range was taken as 100 kHz in all cases. The positive voltage hereafter refers to metal positive and semiconductor negative whereas negative voltage refers to metal negative and semiconductor positive. The devices were subjected to irradiation by high energy heavy ions with ~100MeV gold ions with 3 - 5pna at Inter University Accelerator Centre (formerly known as Nuclear Science Center, NSC), New Delhi. No external bias was applied to the devices during ion beam irradiation. 100MeV gold ions were of our interest for irradiation, to study the effect of radiation induced defects at the interface of the devices due to the electronic energy loss. For the gold ions the electronic energy loss (Se) is greater than the nuclear energy loss (Sn) in a target material [14]. The depth range of these gold ions in our devices, as calculated by the SRIM program, is only 12.81μm which is near the interface region of the M-S junction.

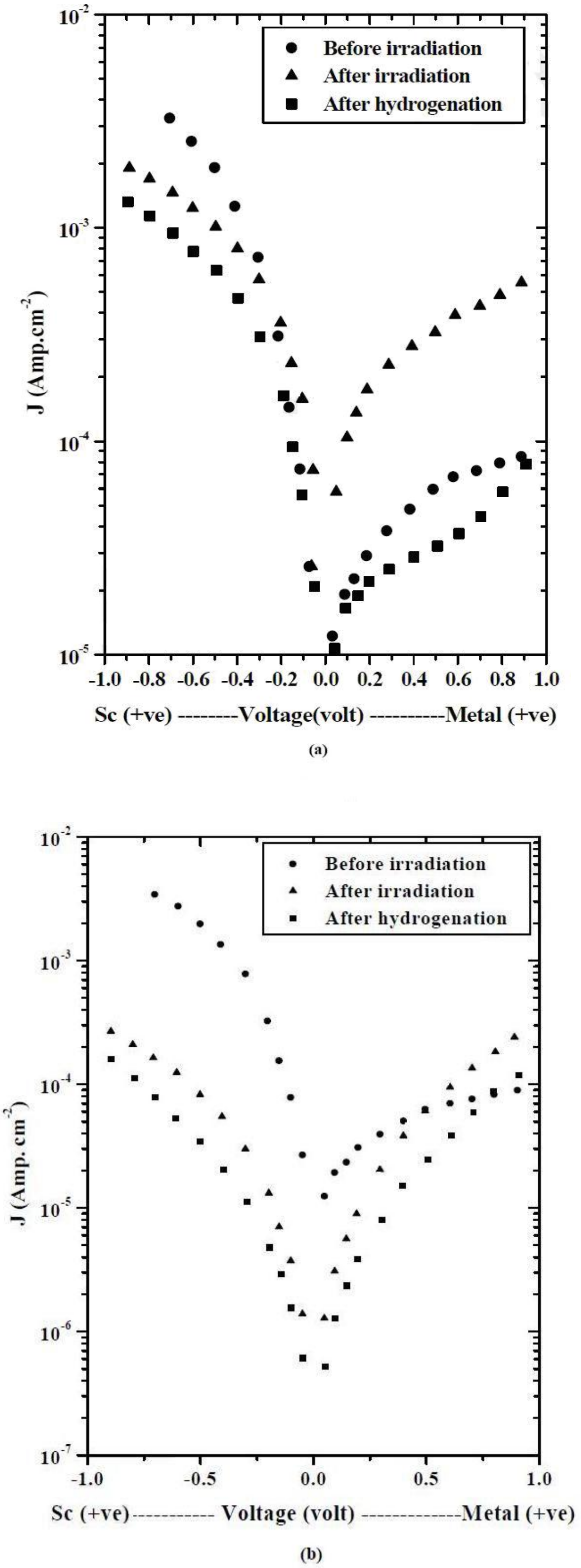
These devices were hydrogenated by keeping them in an evacuated chamber (of vacuum $\sim 10^{-4}$ torr) after the irradiation. For hydrogenation, the devices (without any bias) were kept in a bell-jar chamber which was evacuated then hydrogen gas was introduced in it. The devices were in the hydrogen atmosphere for ~24 hours before being taken out for further measurement. To anneal the devices, a setup attached with rotary pump was made. Annealing of devices was performed in the vacuum of $\sim 10^{-3}$ torr. The annealing studies of irradiated and hydrogenated devices were carried out in the range 100 to 400°C for 30min. After each annealing temperature, the C-V characteristics and I-R spectra were recorded.

3. Results and discussions

In order to study the electronic properties (bulk and interface) of Pd/p-Si devices, J-V and C-V characteristics were carried out. Fig.1a & Fig.1b show the typical J-V characteristics of Pd/p-Si devices before and after the irradiation with fluences 2.6×10^{10} cm^{-2} and 1.5×10^{12} cm^{-2} respectively. Figures(Fig.1a and Fig.1b) also show the J-V characteristics of hydrogenated devices. It is well known that the hydrogen absorbed by Pd, diffuses through interface into the silicon and passivate the dangling bonds and small point defects. It is observed from the Fig.1a & b.

The forward current of the diode decreases after the irradiation. This is indicative of the increase in the resistivity after irradiation. Moreover, hydrogenation does not cause any improvement in the characteristics. It seems that the radiation induced defects are either trapping the majority carriers or/and compensating the carriers to decrease the current flow and increase the resistivity on the irradiation. Trapping of carriers by the defect states gives rise to irradiation induced carrier removal phenomenon. Moreover, hydrogen seems to complex with radiation induced defects to enhance the carrier removal/compensation effect rather than passivating the defects.

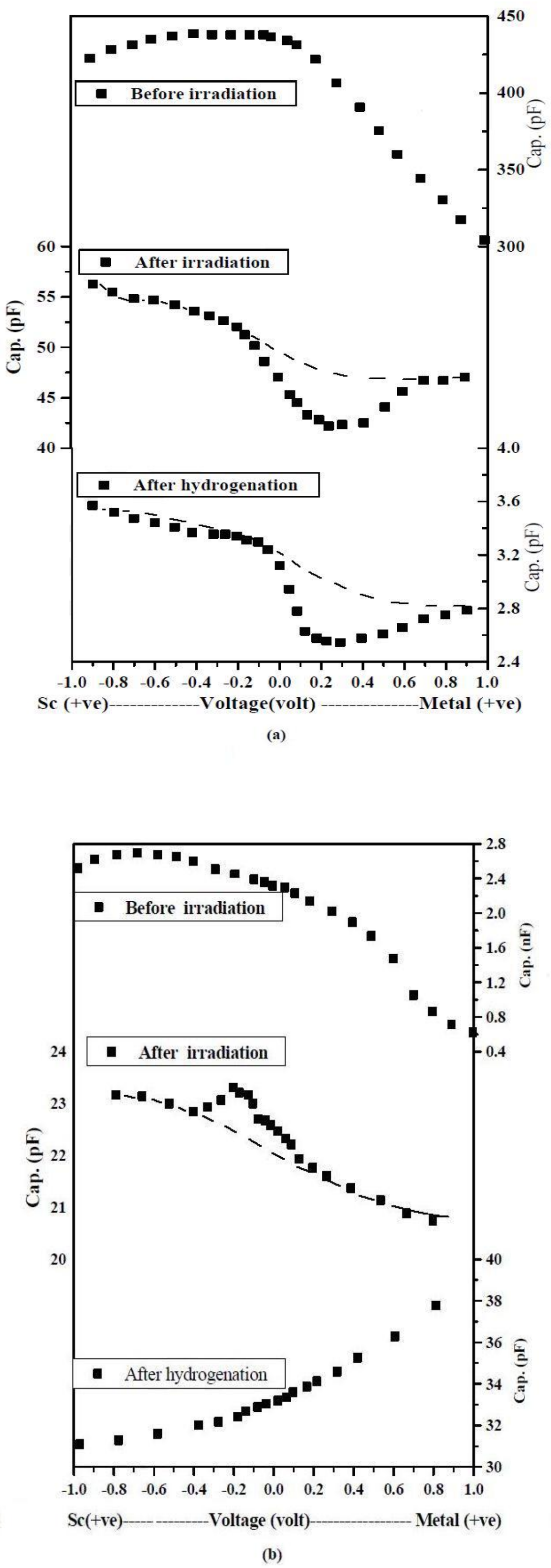
Fig.2a shows the C-V characteristics for Pd/p-Si device before and after the irradiation with fluence 2.6×10^{10} cm^{-2}. It is observed that the capacitance value decreases significantly after the irradiation of the devices. The capacitance is observed to decrease further after the hydrogenation. The C-V characteristics of the devices prior to the irradiation also show the presence of interfacial layer of charges (Fig.2a). The dip in the reverse bias capacitance shows the presence of majority carrier deep traps whereas a dip in the forward bias reflects the presence of minority carrier deep traps [15]. In Fig.2a, the dip represents deep acceptors (electron traps) which are localized near $\sim E_c - 0.33$eV with a peak density $\sim 1.1 \times 10^9$ cm^{-2}. The energy level has been estimated by using the voltage value of the capacitance dip and the barrier height. The density of states has been estimated from the area of the dip on the C-V characteristics. The devices after hydrogenation (Fig.2a) show a similar dip in the C-V characteristics but with a reduced area and hence a reduced density of states of $\sim 7.7 \times 10^8$ cm^{-2}.



(a)

(b)

Fig.1. J-V characteristics of Pd/p-Si diodes irradiated with ~100MeV, Au-ions of fluence a) 2.6x10^{10} cm^{-2}, (b) 1.5x10^{12} cm^{-2}



(a)

(b)

Fig. 2. C-V characteristics of Pd/p-Si diodes irradiated with ~100MeV, Au-ions of fluencies (a) 2.6x10^{10} cm^{-2}, (b)1.5x10^{12} cm^{-2}

The high fluence irradiated devices (Fig.2b) show a similar reduction in capacitance (from nF to pF) and also show the conductivity type change from p-type to n-type on hydrogenation. Moreover, The C-V characteristics of the irradiated and hydrogenated devices are deviated from the usual one and show the presence of deep states (Fig. 2b). The shallow acceptor density estimated from C^{-2} Vs V plots, shows a reduction by two orders of magnitude after the irradiation (The linear portion of C^{-2} Vs V plots has been used to estimate the carrier density). The irradiated devices show a capacitance peak near the forward bias. It represents the presence of deep states which are donor type (hole trap) and the density of these traps has been estimated to be of 4.6×10^{8} cm^{-2} which is located near $\sim E_v + 0.29eV$. These devices show a conductivity type change after the hydrogenation because the C-V characteristics are observed to be reverted for the forward and reverse bias (Fig. 2b). The irradiated and hydrogenated devices were annealed in a vacuum (of $\sim10^{-3}$ Torr) at different temperatures upto 400 °C for half an hour at each annealing temperature. Fig. 3 (and Table-1) shows the C-V characteristics of devices. It has been observed that there is a change in conductivity type at 150 °C (from p-type to n-type) for low fluence (2.6×10^{10} cm^{-2}) irradiated devices. This change is due to 'reverse annealing' effect which is responsible to decrease the carrier compensation [16]. On further annealing at higher temperature, the devices {irradiated with low (2.6×10^{10} cm^{-2}) and high (1.5×10^{12} cm^{-2}) fluence and hydrogenated} change their conductivity type at different temperatures (Table-1).

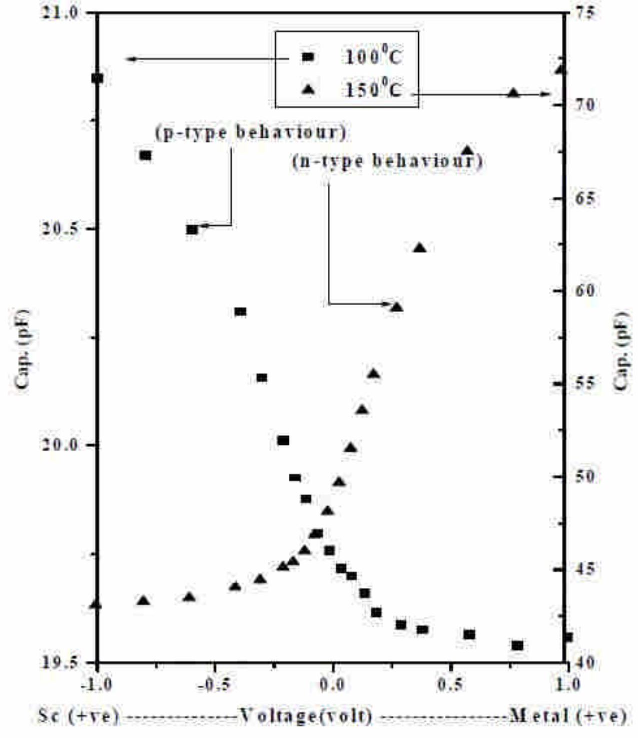


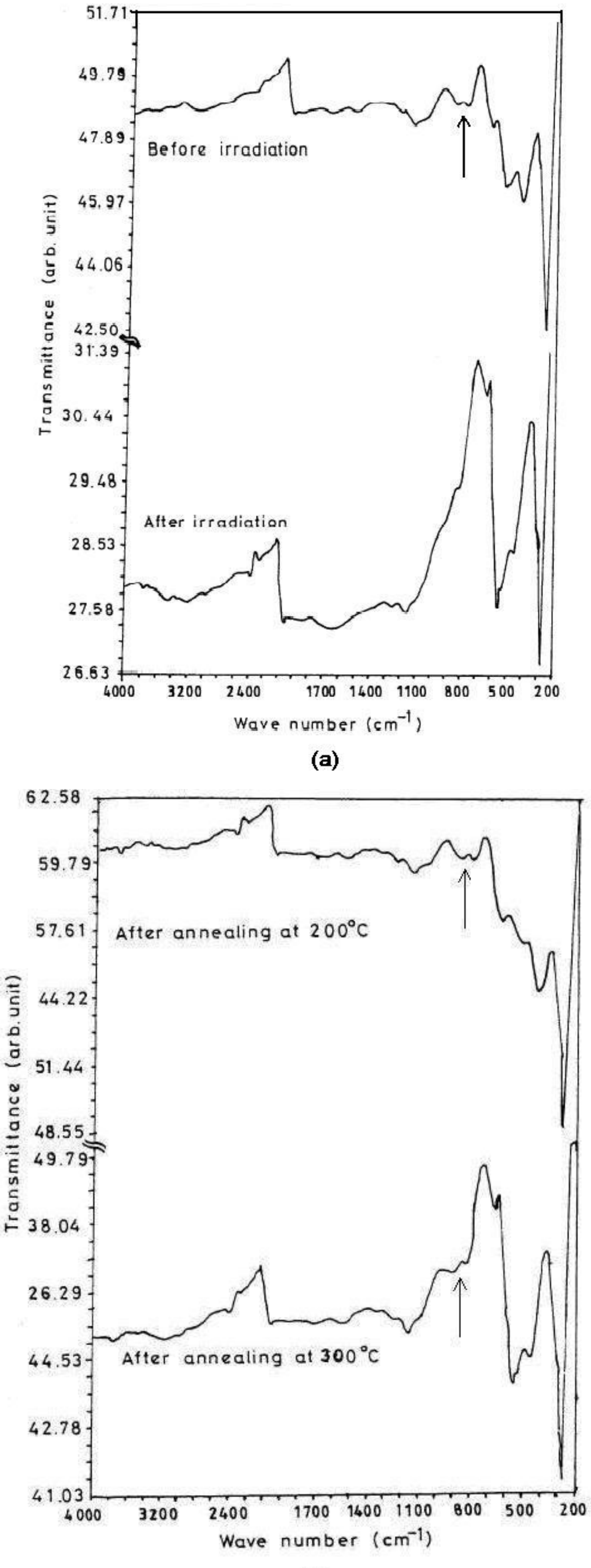
Fig. 3. C-V characteristics of diodes annealed at temperature 100°C and 150°C after the irradiation and hydrogenation.

The devices finally change to p-type again (from n-type) at 400 °C after passing through a heavy compensation at350 °C. It seems that the recovery of conductivity type on annealing, consists, initially a reduction in n-type concentration followed by type conversion and gradual increase in p-type concentration. The annealing behavior of irradiated and hydrogenated devices may be due to the movement of interstitial impurities such as carbon, oxygen [17]. These impurities may cause the configurations of radiation induced defects to behave differently for changing the observed change in conductivity type.

The infrared studies on the swift heavy ion irradiated (1.5×10^{12} cm^{-2}) devices have been performed before and after each annealing steps to understand the defect complexes involved in the radiation damage and annealing processes. It is observed that the intensity of the vibrational absorption bands (Fig. 4a) are changing with temperature. The change in intensity of vibrational bands show the movement of impurities which are complexing with radiation induced defects. It is interesting to observe that the absorption band near (900 ± 20) cm^{-1} disappears after the irradiation and reappear after annealing at 200°C (Fig. 4b) with improved intensity. Its changing configuration has also been seen in spectra after annealing at 300 °C (in terms of area of absorption peak) (Fig.4b). The observed band has been attributed to VO_2 complexes [18]. These complexes are significant radiation damage defects which may play the role for carrier compensation/removal phenomenon at different annealing temperature to cause the observed effects (Table 1).

Table 1. Annealing Behavior of irradiated and hydrogenated Pd/p-Si devices from C-V studies

Annealing Temperature (°C)	Low fluence ($2.6\times10^{10}cm^{-2}$) irradiated devices	High fluence ($1.5\times10^{12}cm^{-2}$) irradiated devices
After irradiation (at room Temperature)	p-type	p-type
After Irradiation and Hydrogenation (at room Temperature)	p-type	n-type
100°C	p-type	n-type
150°C	n-type	n-type
200°C	n-type	n-type
250°C	n-type	Highly compensated
300°C	p-type	n-type
350°C	---------	Highly compensated
400°C	---------	p-type



(a)

(b)

Fig. 4. I-R Spectra of Pd/p-Si devices irradiated with 100 MeV gold ions of fluence 1.5×10^{12} cm^{-2} (a) Before and After Irradiation, (b) After annealing at 200 °C and 300 °C.

The decrease in conductivity or increase in resistivity of the devices after the irradiation can be understood as the loss of current carriers or decrease of majority carrier density and/or decrease of carrier mobility. The carrier mobility is reduced up to some extent by the presence of radiation induced defects (acting as deep levels) [19] but the observed increase of resistivity on the irradiation is high enough than expected from the aforesaid possible change in mobility. The loss of carriers after the irradiation is also termed as the carrier removal phenomenon due to the radiation induced defects. The radiation induced defects acting as majority carrier traps which reduce the effective current carriers and hence may work as carrier removal centers. The device resistance is a series combination of metal semiconductor interface, the bulk resistance of the semiconductor substrate and the bottom ohmic contact. Thus, the observed conductivity or increased resistivity after the irradiation is a net effect of the entire device.

The capacitance of the devices is controlled by the charge exchange in the depletion region spread near the metal/semiconductor interface. However, it is worth pointing out that the capacitance is also affected by the series resistance of the diodes which depends on the bulk resistance of the semiconductor substrate of the device. Carrier removal has been found to be a significant characteristic of the displacement damage [20]. It seems that the high energy heavy ions irradiation of our devices cause the displacement damage to feature the carrier removal phenomenon to increase the resistivity on the irradiation. The measured capacitance depends upon the emission of trap (e) and rate of change of applied a.c. signal (w) for measuring the capacitance. Most of the charge captured by 'slow traps' for which w>>e is retained in the depletion region during the measurement and so contribute to the measured capacitance. Whereas the traps for which e>>w at the measurement temperature, referred to as 'fast traps', do not affect the measured capacitance significantly [21]. The observed majority carrier traps (acting as deep acceptors at E_c – 0.33eV) in low dose (2.6×10^{10} cm^{-2}) of gold ion irradiated devices are from a depletion depth of ~3.0μm. The density of these traps (1.1×10^{9} cm^{-2}) is not sufficient enough to cause the observed carrier removal in the irradiated devices. It seems that it could be possible to visit these localized states by the capacitance signal of the device, because the depletion region widens deep due to the reduced capacitance (from nF to pF range) on irradiation. The depletion width (of ~3.0 μm) is shallower than the range of the irradiated ions of gold in silicon (12.81μm from SRIM calculation). Thus the observed electronic states may be related to the damage defects caused by the electronic energy loss of the incident ions in the target lattice (of silicon). In high energy irradiated silicon, the formation of di-vacancy [22] has been found to be more probable. The di-vacancies can be formed by the combination of vacancies. These di-vacancies become mobile at temperatures between 200°C - 300°C and may complex with impurities forming V_xO_y

complexes [23]. The mono vacancy produced by irradiation either trapped by the O_i to form V-O, annihilate by silicon or combine with other to form di-vacancy.

4. Conclusion

Electronic properties of the Pd/p-Si devices have been investigated as a function of irradiation fluence, hydrogenation and annealing temperatures. We observed that the decrease in the current density and capacitance values reflects the widening of the depletion region due to the irradiation induced defects. The hydrogenation of irradiated devices also shows the reduction because of the radiation induced defects complex with hydrogen to cause the compensating effect. The observed annealing effects are attributed to the net effect of carrier removal and/or carrier compensation phenomenon. It seems that the vacancy/multi-vacancy hydrogen complexes configure differently as a donor or acceptor state to cause the conductivity type change on annealing at different temperatures. It is significant to mention here that the present I-R absorption studies show the absorption bands for VO, VO_2 near (900 ± 20) cm^{-1}. The observed change in conductivity after annealing at different temperatures seems related to annealing of V-O centers which is changing its configuration with temperature.

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[*] Corresponding author: pandeysp72@rediffmail.com