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### Topic Review:

# Modulating properties by light ion irradiation: From novel functional materials to semiconductor devices

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#### **Abstract:**

In this review, the application of light ion irradiation is discussed for tailoring novel functional materials and for improving the performance in SiC or Si based electrical power device. The deep traps and electronic disorder produced by light ion irradiation can modify the electrical, magnetic and optical properties of films, e.g. dilute ferromagnetic semiconductors and topological materials. Additionally, benefiting from the high reproducibility, precise manipulation of functional depth and density of defects, as well as the flexible patternability, the helium or proton ion irradiation has been successfully employed in improving the dynamic performance of SiC and Si based PiN diode power devices by reducing their majority carrier lifetime, although the static performance is sacrificed due to deep level traps. Such a trade-off has been regarded as the key point to compromise the static and dynamic performances of power devices. As a result, herein the light ion irradiation is highlighted in both exploring new physics and optimizing the performance in functional materials and electrical devices.

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## Introduction

Ion beam has presented a variety of useful functions in the field of semiconductors, acting as the state-of-the-art tool for both basic research and industry. Particularly, it is worth noting that ion implantation has been integrated as one of the most crucial processes in modern IC industry <sup>1, 2</sup>. Recently, a number of novel functional semiconductors have been successfully fabricated by ion implantation at high fluence and ultra-fast annealing <sup>3-10</sup>. For such instances, the implantation is highlighted to overcome the obstacle of solubility limit of impurities in semiconductors, which is always treated as the main challenge of conventional equilibrium methods.

In addition to the above-mentioned well-known doping contributions introduced by implanted ions themselves, point defects in the semiconductor matrix are spontaneously produced point defects in the semiconductor matrix are spontaneously produced due to the collisions between incident ions and the matrix atoms. The interaction between implanted ions and target atoms could be briefly described as below: By undergoing collisions with the electron system and the nuclei of the target matrix, the impinged ions gradually lose the kinetic energy. In the very beginning, the kinetic energy lose is mainly caused by the electronic stopping (excitation and inelastic atom ionization), which dominates in the high energy regime. Accordingly, this part of transferred energy is partially dissipated by phonons, however the displacement of lattice atoms seldomly happens. Afterwards, upon penetrating into deeper depth, the implanted ions start to confront nuclear stopping due to their low kinetic energy, in which the displacement of atoms starts to dominate and even leads to a cascade of recoiled atoms. At this moment, the point defects start to accumulate. The schematic of relative lose of kinetic energy is shown in Fig. 1 to make a comparison between electronic and nuclear stopping processes with their dependence on ion kinetic energy <sup>11, 12</sup>.

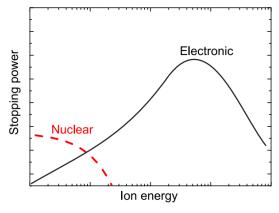


Figure 1 (Color online) Schematic of the cross-section for electronic and nuclear stopping processes as a function of ion energy <sup>12</sup>.

Actually, the above-mentioned point defects can provide additional functionalities

in semiconductor materials. Particularly, light ions, e.g. proton, helium as well as some other ions whose atomic numbers are relatively small, are beneficial for a better access of thick films/devices as well as for a gentle control of amount of defects without inducing amorphisation. Therefore, light ion irradiation is becoming more and more attractive in both of condense matter physics and semiconductor techniques. From the basic research viewpoint, the generated various vacancies or interstitials act as potential disorder thus in principle affect the electrical-transport properties, e.g. carrier mobility, therefore highlighting the contribution of Anderson localization <sup>13</sup>. On the other hand, the introduced defects cause new energy levels locating in the bandgap, and contribute intensively to the transport behavior, mostly by tuning carrier concentration <sup>14</sup>. Although several avenues have been explored to involve the point defects in functional material matrix, e.g. non-stoichiometric growth, it is worth mentioning that the light ion irradiation is still advantageous by several merits as below:

- a) High throughput and reproducibility;
- b) Precise control of the density of generated defects and their depth profile by tuning the implantation fluence and energy;
- c) Flexible pattern for devices by combining conventional semiconductor industry techniques, e. g. photolithography and mask.

In this short review, we only focus on the application of light ion irradiation in tailoring the electronic properties of emerging functional materials <sup>15, 16, 17, 18</sup> and in modifying the dynamic performance of semiconductor power device <sup>19, 20</sup>. The other applications such as doping semiconductors and "smart cut" <sup>21, 22</sup> are not covered.

### 1. Manipulating defects in conventional and novel functional materials

## 1.1 Tuning the Fermi level in dilute ferromagnetic semiconductors

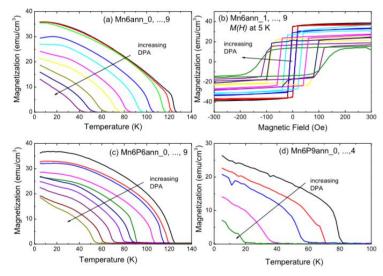


Figure 2 (Color online) Magnetic properties after introducing hole compensation by ion irradiation. The ion fluence was increased in linear steps. (a), (c), and (d) show the temperature dependent magnetization

for different samples, while (b) shows the magnetic hysteresis for sample Mn6ann (GaMnAs) for various ion fluences. The temperature-dependent magnetization is measured at a small field of 20 Oe after cooling in field. One observes an increase in the coercive field  $H_{\rm C}$  when  $T_{\rm C}$  and the remanent magnetization decrease. The arrows indicate the increase of DPA from 0 to  $2.88 \times 10^{-3}$ . In each panel, the black line is the result for the nonirradiated sample. Figure is from Ref. <sup>15</sup>.

Dilute ferromagnetic semiconductors (DFSs) have been viewed as the one of the most fancy topics in the past several decades. Due to the nature of hole-mediated ferromagnetism in DFSs, any methods used in tuning carrier concentration <sup>23</sup>, e.g. electrical gating or co-doping, can be used to modify ferromagnetic properties or explore the interplay between electrical and ferromagnetic features. Thus as expected, the light ion irradiation just fulfills the requirement of carrier density modification<sup>24,25</sup> by compensating carriers through introducing deep level traps, afterwards creating platform to understand the physics in DFSs.

Since the discovery of DFSs, the mechanism of hole-mediated ferromagnetism is always placed in the central of argument stage where the competition between p-d Zener model and the impurity model never stops. In p-d Zener model the randomly distributed Mn moments are bridged by the itinerant valence band holes <sup>23</sup>, while the localized holes in the isolated impurity band dominate the mediation according to the impurity band model <sup>26</sup>. Expectedly, ion irradiation allows the flexible manipulation of carrier concentration, by which the Fermi level could be shifted in a large range from the valence band towards the bandgap. This helps a lot to explore the interplay between carrier localization and magnetism in DFSs. Before the irradiation, H<sup>+</sup> plasma is initially proposed to control ferromagnetism in DFSs by S. T. B. Goennenwein et al.<sup>27</sup>: The H<sup>+</sup> plasma successfully drives the GaMnAs from ferromagnetic state with ~70 K Curie temperature into paramagnetic state by compensating holes. Enlightened by the idea of H<sup>+</sup> plasma, light ion irradiation was utilized to intentionally produce the tapping defects in GaMnAs, and magnetization and magneto-transport were both manipulated <sup>28</sup>. In 2016, a more systematical picture in irradiated GaMnAs was depicted <sup>15</sup>: By increasing fluences, irradiation results in a raised lattice disorder, quantified by displacement per atom (DPA), leading to an enhanced carrier compensation. As a result, the system changes from original metallic to insulating state, confirming the gradual departure of the Fermi level from valence band into the bandgap <sup>15</sup>. For magnetic properties, it is observed that the saturation magnetization, remanent magnetization as well as Curie temperature decrease upon increasing DPA, which is in agreement with the description of p-d Zener model. As shown in Figure 2, the temperature dependent magnetization of GaMnAs<sub>0.94</sub>P<sub>0.06</sub> as well as GaMnAs<sub>0.91</sub>P<sub>0.09</sub> under different irradiation fluences is displayed: upon increasing the DPA by raising irradiation fluences, the temperature dependent magnetization curve gradually deviates from the mean-field theory described convex shape, which indicates that the system is away from the global ferromagnetism. It is worth noting that by benefiting from carefully tuning irradiation fluence, it is possible to capture detailed statues of the whole evolution process, further helping to analyze the correspondence between carrier localization and magnetization reduction. As a result of the irradiation induced hole-compensation, the Fermi level shifts back to the bandgap, meanwhile magnetism is gradually deviated from the global ferromagnetism due to the weakened hole mediation. Consequently, the nano-scaled electronic phase separation appears and the long-range ferromagnetic coupling is interrupted. In addition to the reduced magnetism, it has been also verified that the uniaxial magnetic anisotropy is manipulated by irradiation, through shifting the Fermi level between the splitting valence band <sup>25</sup>. The successful anisotropy modification again confirms the validation of *p-d* Zener model.

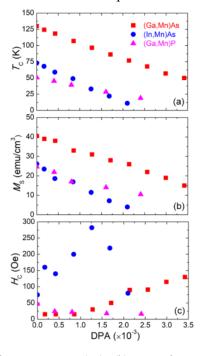


Figure 3 (Color online) (a) Curie temperature ( $T_C$ ), (b) saturation magnetization ( $M_S$ ) as well as (c) coercive feld ( $H_C$ ) for the magnetic easy axis at 5K versus DPA for (Ga,Mn)As (squares), (In,Mn)As (circles) and (Ga,Mn)P (triangles). <sup>16</sup>

Besides the most widely studied GaAs based DFSs, the proton irradiation can also stabilize the Fermi level in relatively different positions in the bandgap in various III-V matrixes  $^{29}$ . Therefore, it is easy to imagine that the same irradiation condition would perform different compensation effect in various matrixes, further contributing discriminately to the magnetism manipulation. As expected, the above-mentioned deduce was confirmed by our previous work that the same DPA results in the different magnetism-modification in GaMnAs, InMnAs and GaMnP: As shown in Figure 3, the DPA dependent saturation magnetism and  $T_{\rm C}$  curves show different slopes, which unambiguously confirm that the produced defects work differently in different III-Mn-V compounds.

## 1.2 Generating potential disorder in topological materials

In addition to modify the Fermi level by introducing carrier compensation, in some cases, the structural or potential disorders caused by irradiation induced defects can significantly influence electrical-transport properties even though the carrier concentration remains constant<sup>30</sup>. With the presence of disorder, the mean free path is disturbed due to the break of long-range Bloch extended potential, consequently the effect of Anderson localization is largely enhanced and carriers become more localized <sup>31</sup>. Actually, in some systems both of the carrier compensation and potential disorder cooperatively change magneto-transport properties. Thus ion irradiation can be employed as a useful tool to investigate the above mentioned two contributions, particularly in recent topological insulators/superconductors <sup>32-35</sup>.

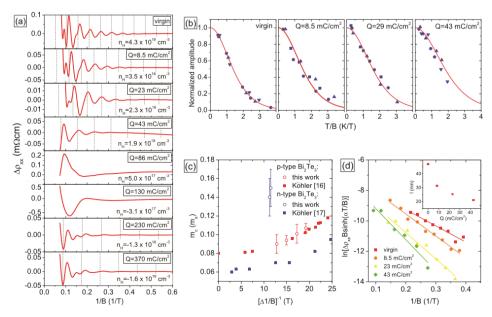


Figure 4 (Color online) (a) Oscillating part of the resistivity  $\Delta \rho_{xx}$  at 1.9 K for B//c as a function of inverse magnetic field 1/B for different irradiation doses. (b) Temperature dependence of the oscillation amplitude with solid lines representing the fits obtained using the equation of  $\Delta \rho_{xx} \left(\frac{T}{B}\right) = \frac{\alpha T}{Bsinh(\alpha T/B)}$ . Different symbols correspond to the analysis of different Landau levels, i.e., peaks at different 1/B positions. In order to compare the temperature dependence of different peaks, the oscillation amplitudes have been normalized to the value of the fit for 1/B  $\rightarrow$  0. (c) Cyclotron masses  $m_C$  as function of the inverse oscillation period  $[\Delta(1/B)]^{-1}$ . (d) Dingle plots at T =1.9 K and inset showing the mean free path l as a function of irradiation dose Q  $^{32}$ .

By borrowing the concept of Fermi level tuning in DFSs, it has been tried to test the valid of manipulating carrier type or concentration through irradiation in a canonical topological insulator  $\rm Bi_2Te_3$   $^{32}$ . Upon increasing electron irradiation fluences, the upshift of the Fermi level is clearly observed together with a turnover of conductivity from p to n type. The detailed evolution of the electrical transport behavior can be explored by Shubnikov-de-Haas oscillation which is popular in systems with high carrier mobility: With increasing magnetic field, the movement of spin-split Landau levels causes the periodical oscillation of resistance, including both longitudinal resistance

 $(\rho_{xx})$  and Hall resistance  $(\rho_{xy})$ . By carefully analyzing the period and magnitude of the oscillation through fast Fourier transformation, it is possible to obtain the effective mass, the carrier density as well as the mean free patch according to the standard Lifshitz-Kosevich theory <sup>36</sup>. As shown in Figure 4(a), with the dependence of irradiation fluences from 8.5 to 370 mC/cm<sup>2</sup>, the oscillation of  $\Delta\rho_{xx}$  (obtained by subtracting the background magnetoresistance) is tuned and accordingly the carrier concentration changes from  $4.3 \times 10^{18}$  (hole) to  $-1.6 \times 10^{18}$  /cm<sup>3</sup> (electron), presenting the donor characteristic of electron irradiation induced defects which are computationally assumed as Te vacancy clusters and Te<sub>Bi</sub> antisite defects <sup>37, 38</sup>. It is worth noting that the donor-like defects are produced not only by electron irradiation, and similar phenomenon has been observed in proton irradiated Bi<sub>2</sub>Te<sub>3</sub> as early as in 1966, although at that time the Te interstitial was deduced as the origin<sup>39</sup> and subsequently observed by transmission electron microscopy <sup>40</sup>. It can be concluded that the modification of carrier concentration by ion irradiation works not only in semiconductors, but also in high mobility topological materials, which expands the application matrix of ion irradiation.

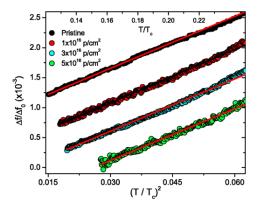


Figure 5 (Color online) Low-temperature variation of the London penetration depth  $\Delta\lambda(T)$  in a single crystal of Nb<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> for multiple values of cumulative irradiation dose vs reduced temperature squared  $(T/T_C)^2$ . The linear fits (red, black lines) indicate quadratic behavior. As the dose increases, the temperature dependence remains quadratic, indicative of point nodes in the superconducting gap. Data are offset vertically for clarity of presentation. The top axis shows the corresponding  $T/T_C$  values <sup>41</sup>.

As the above discussion, the irradiation induced defects not only compensate carriers, but also produce electrical disorder which violates the highly ordered Bloch potential. It is well known, in a material with low mobility the contribution of compensation is mainly in charge, however in a high mobility system the disorder effect starts to dominate. As described in Figure 4(d), the mean free path reduces in half and saturates when the fluence is 43 mC/cm<sup>2</sup>, indicative that the contribution of electrical disorder is comparable with that from the Fermi energy shift. Subsequently, such a disorder is treated as a meaningful tool to investigate the disorder contribution in other topological materials, e.g. Nb<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub><sup>41</sup> and Sn<sub>1-x</sub>In<sub>x</sub>Te<sup>42</sup>. For instance, according to the study by M. P. Smylie et. al<sup>41</sup>, due to the symmetry-protection, the superconducting

state in doped topological NbBi<sub>2</sub>Se<sub>3</sub> surprisingly presents its robust resistance to disorder-induced electron scattering which is introduced by irradiation. As shown in Figure 5, although the superconducting transition temperature  $T_{\rm C}$  is gradually suppressed upon raising proton-irradiation fluences, but both pristine and irradiated samples show quadratic dependence of London penetration depth versus temperature, which always happens in a clean system with linear quasi-particle dispersion around the point nodes in the superconducting gap <sup>41</sup>. Meaningfully, such a result suggests that all samples are naturally clean even though they have been irradiated under a variety of fluences, indicative of the appearance of the symmetry protected point nodes in Nb<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub>. With the aid of irradiation, such an unexpected phenomenon was firstly seen and demonstrated the robustness of unconventional superconductor against the non-magnetic disorder, which means that the topological superconducting can be achieved in rather dirty systems.

### 2. Manipulating the dynamic properties in semiconductor power devices

The explosion of electric power employment, particularly the preliminary success of electric-vehicle is raising the unprecedented demand for p-n diode power device. Among various performances of devices, the switching speed (in particular switch-off) is becoming crucial for evaluating the comprehensive performance, particularly in high-frequency applications. Such an expectation starts the employment of light ion irradiation technique to tune the lifetime of majority carriers. Although some conventional approaches like diffusion life-killers have been maturely used in Si based power device, some shortages e.g. short diffusion length or low sensitivity, still prohibit their utility in SiC based devices <sup>43</sup>. Additionally, by carefully playing the irradiation energy combined with photolithography, the ion irradiation allows precise and flexible modulation of carrier recombination in both in-plane and depth profile at micro or nanoscale. However, it still has to admit that the speed up of the device achieved by this approach always accompanies with the sacrifice of blocking voltage, carrier mobility, and some other on-state static performance due to introduced various defects <sup>20, 44, 45</sup>. Thus unfortunately such modulation is treated as a trade-off between static and dynamic prerequisites. Nevertheless, part of irradiation caused defects still can be cured by thermo-treatments, which will partly recall the device statue before the irradiation<sup>46</sup>. As a result, such a competition playground of irradiation vs. thermo-treatment works flexibly on tracking the optimal device performance. As discussed in former sections, various types of defects appear in irradiated Si and SiC matrix, furthermore influencing differently on their device performance. This part will be mainly discussed in the next sections.

## 2.1 SiC semiconductor and SiC power device

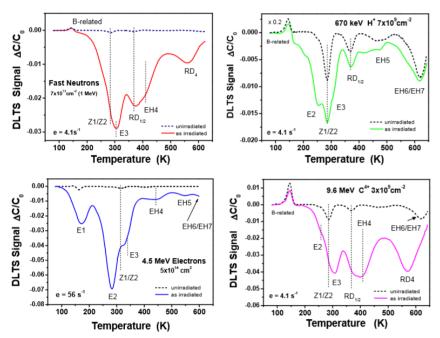


Figure 7 (Color online) DLTS spectra of 4H-SiC n-type epilayer irradiated with fast neutrons (upper left), 4.5 MeV electrons (lower left), 670 keV protons (upper right), and 9.6 MeV carbon ions (lower right). First temperature scan, rate window 4.1 s<sup>-1</sup> (neutron, proton and carbon irradiation) and 56 s<sup>-1</sup> (electrons).<sup>47</sup>

It has been revealed that distinctive sets of defects in SiC are produced by irradiation, and the deep level transient spectrum (DLTS) is often employed to identify deep level defects. As the study from P. Hazdra et al. shown in Fig. 7, the results are present in fast neutrons, electrons, protons as well as carbon ions irradiated n-type 4H-SiC <sup>47</sup>, and different deep traps are introduced in the bandgap. As shown in Fig. 7, the E<sub>3</sub> and E<sub>2</sub> deep levels are mainly caused by fast neutrons (1 MeV, 7×10<sup>13</sup> /cm<sup>2</sup>), carbon ions (9.6 MeV,  $3\times10^9$  /cm<sup>2</sup>) as well as electrons (4.5 MeV,  $5\times10^{14}$  /cm<sup>2</sup>) while the  $Z_{1/2}$  trappers are caused by proton irradiation (670 keV,  $7 \times 10^9$  /cm<sup>2</sup>). The origin of such a distinction is the different collision effect between the implanted ions and the host matrix, leading to various defect complexes in the sample, and accordingly the induced traps locate in different levels in the bandgap. Most of them work as the carrier trap centers in the matrix and reduce the lifetime of carriers, whereas only the thermo-stable ones are preferential when being considered functionally and stably in device. Many researchers have focused on the thermo-behavior of various traps, and finally the  $Z_{1/2}$  is successfully qualified because of its persistence at the temperature even above 2000 °C <sup>48-50</sup>. Additionally, the advantage as a prominent lifetime monitor also places  $Z_{1/2}$  in the central of lifetime engineering stage<sup>51</sup>. From the fundamental research point of view, plenty of efforts have been made to clarify the birth of  $Z_{1/2}$  defects, and various hypothesizes have been proposed. In the very early stage, the  $Z_{1/2}$  defects were found in the nitrogen doped SiC and the correlation between the trap density and N dopant was deduced  $^{52}$ , accordingly the most proper candidate model of  $Z_{1/2}$  trap was

formulated as the configuration of an nitrogen atom neighboring with dicarbon interstitials  $^{53}$ . However, the subsequent experiment ruled out such an assumption in terms of observing the dependence of  $Z_{1/2}$  concentration in P doped SiC when the density of doping phosphorus is almost one magnitude higher than that of nitrogen. Interestingly, such an experiment excluded the possible participation of nitrogen in the complex  $^{54}$ . According to subsequent studies, it is found that the  $Z_{1/2}$  defect is a kind of intrinsic defect complex in the SiC matrix, and it is caused by two possible configurations: (i) silicon vacancy combined with carbon interstitial ( $Si_v+C_{int}$ ) or (ii) carbon vacancy neighbored with silicon interstitial ( $C_v+Si_{int}$ ). More and more experimental results favor the latter model, e.g. by carbon implantation  $^{55}$  or annealing of electron irradiated SiC. Even though a lot of attention has been paid to this topic, the clarification of  $Z_{1/2}$  defect is still limited. Nevertheless, such a fact does not shake its role as carrier life-time manipulator in SiC devices.

In order to modulate the carrier lifetime, several approaches have been employed to demonstrate or excavate the function of  $Z_{1/2}$  before the light ion irradiation technique is imported: The annihilation of  $Z_{1/2}$  defects extends the carrier lifetime. For instance, several studies have shown that the carrier lifetime in carbon-implanted SiC are increased by high temperature annealing 55, 56. The lifetime was also pronouncedly enhanced in as-grown SiC layers by high temperature annealing <sup>49</sup>. In addition, another alternative method to promote the lifetime through killing  $Z_{1/2}$  is the thermo-oxidation. For example, according to studies from T. Kimoto, through eliminating the  $Z_{1/2}$  density, carrier lifetimes were prolonged from 1.1 µs and 0.73 µs to 33.2 µs and 1.62 µs, respectively, by thermo-oxidation 46, 57. On the contrary, it is also meaningful to intentionally build up  $Z_{1/2}$  defects in some cases where a short lifetime is required, e.g. high frequency p-n junction. As shown in Fig. 7, the proton irradiation (sometimes electron irradiation) which is an effective way for producing Z<sub>1/2</sub> is strongly recommended. Actually, a series of defects are produced by proton irradiation together with  $Z_{1/2}$  trap, as displayed in Table I. However, mainly the  $Z_{1/2}$  and EH<sub>6/7</sub> can survive after the subsequent low temperature annealing, and improve the performance of p-njunction SiC device <sup>19, 58</sup>. As presented in Fig. 8, several signals at around 300, 440, 570 and 660 K appear in irradiated samples, but are absent in the as-grown one, confirming the vacancy-production via proton irradiation. However, despite the subsequent annealing cures the defects of EH<sub>1</sub> and EH<sub>3</sub>, intensive Z<sub>1/2</sub> and EH<sub>6/7</sub> peaks still can be observed at around 300 and 660 K, which definitely verifies their thermostabilization, thus determines their qualification of being life-time tailor.

Table I Parameters for proton irradiation induced deep levels in *n*-type SiC

Level	Energy [eV]	Literature
$T_1$	E <sub>C</sub> - 0.17	19, 59
$\mathrm{EH}_1$	$E_{\rm C}$ - 0.42	19, 58, 60, 61
$Z_{1/2}$	$E_{\rm C}$ - $0.66$	19, 46, 49, 56, 58, 62
$EH_3$	$E_{\rm C}$ - $0.72$	19, 47, 58, 61
$EH_5$	$E_{\rm C}$ - $0.80$	48
$T_2$	$E_{\rm C}$ - 1.41	59
EH <sub>6/7</sub>	E <sub>C</sub> - 1.64	48, 63

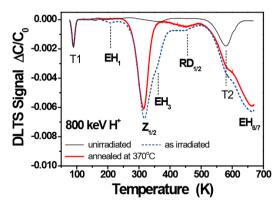


Figure 8 (Color online) DLTS spectra of *n*-base of the 4H-SiC PiN diode measured before (black thin) and after (short-dashed) irradiation with 800 keV protons to a fluence of  $5\times10^9$  /cm<sup>2</sup> and after annealing at  $370^{\circ}$ C (red thick). <sup>58</sup>

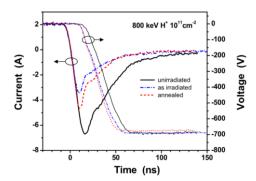


Figure 9 (Color online) Reverse recovery of the 2 A/10 keV SiC PiN diode measured before (solid line) and after irradiation (dashed-dotted line) with 800 keV protons to a fluence of  $1\times10^{11}$  /cm and after subsequent 1 hour annealing at 370 °C (dash line) <sup>19</sup>.

As the above discussion,  $Z_{1/2}$  locates at about 0.44 eV below the bottom of the conduction band, acting as the main local lifetime killer in terms of its large capture cross section for both electrons and holes. When  $Z_{1/2}$  centers are placed in the *n*-region of *p-n* diode junction, the electrons (majority carriers) are strongly compensated in the defect-profiled space, therefore speeding up the device turn-off process. On the basis of the study from P. Hazdra et al. <sup>19, 58</sup>, the proton irradiated 10 kV/2 A PiN diode SiC chips under fluence of  $1 \times 10^{11}$  cm<sup>2</sup> at an 800 keV energy presents 2.5 times reduction of reverse recovery charge when compared with the unirradiated one. As shown in Fig.

9, it is seen that the maximum of the reverse recovery current cuts in half accompanied with a faster and softer switch-off, even though the subsequent annealing partly compensates the irradiation contribution. In addition to reverse recovery waveforms, the open circuit voltage decay (OCVD) is also employed to evaluate the high-level lifetime ( $\tau_{\rm HL}$ ) which is calculated from the slope of dV/dt response, which manipulates the time dependent term of the post injection voltage <sup>64</sup>. As shown in Fig. 10, the irradiated device exhibits a larger slope in the quite initial recovery part, while it negligibly contributes to the slope of the rest part. According to the inset of Fig. 10, upon increasing the irradiation fluences to  $1 \times 10^{10}$  /cm<sup>2</sup>, the  $\tau_{\rm HL}$  is successfully tuned from around 2.8  $\mu$ s down to around 1.6  $\mu$ s, but it saturates when the fluence continues to increase. Note that to achieve such fast switch-off it is necessary to place the defected region at the anode side of the *n*-base in the PiN structure, which is similar as in silicon based *p-n* junction and will be reviewed in the next section.

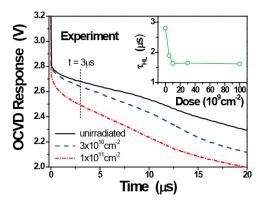


Figure 10 (Color online) Measured OCVD response of 4H-SiC PiN diodes irradiated with different fluences of 800 keV protons. The value of high-level lifetime  $\tau_{HL}$  (extracted at  $t=3~\mu s$ ) for different irradiation fluences are shown in the inset. <sup>58</sup>

In addition to the most wanted  $Z_{1/2}$  type defect, the SiC based p-n device is unavoidably affected by other various type defects, of which the most crucial one is EH<sub>6/7</sub> whose thermo-stabilization is at the same level as  $Z_{1/2}$ . EH<sub>6/7</sub> lies 1.64 eV below the bottom of conduction band (even in the center of the bandgap), much deeper than  $Z_{1/2}$ . As a consequence, they work as charge producer in the space charge region, leading to the diode leakage (off state losses) in irradiated devices. Another negative effect brought by deep level traps is the increase of the forward voltage drop due to the compensation induced electron reduction, and it has been observed in a set of various SiC based devices, e.g. PiN diode<sup>19</sup>, MPS power diode <sup>20</sup> as well as JBS diode <sup>45, 47</sup>. In summary, when the proton irradiation is employed, it is necessary to trade off the balance between dynamic and static performance according to the requirement.

## 2.2 Si semiconductor and Si power device

Despite the fact that many alternative candidates e. g. SiC or GaN, have been

attracting more and more attention, silicon still occupies the main part of power device market due to its mature industrial process. Thus, it is meaningful to review the manipulation of silicon as well as the corresponding device by light ion irradiation. Indeed, the irradiation contribution to silicon devices initiated the followed-up activities in SiC diodes, including IGBTs 65, PiN diode power device 66-68, as well as power thyristors <sup>69, 70</sup>: tuning the lifetime of majority carriers through producing deep level traps. Actually, according to studies in the past several decades, irradiation induced defects in silicon have been fully explored, e. g. E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>, E<sub>4</sub>, E<sub>5</sub>, E<sub>6</sub> as well as E<sub>7</sub>, and detailed information is displayed in Table II. As discussed in former sections, the capture cross section and thermo-stability are both treated as key criteria to evaluate the ability as lifetime-modulator. Overall, two types of defects which respectively locate 0.167 eV (from vacancy-oxygen pair VO<sup>-/0</sup>, defined as E<sub>1</sub>) and 0.436 eV (from divacancy  $V_2^{-/0}$ , defined as  $E_5$ ) below the bottom of conduction band are most important for tuning carrier lifetime. As displayed in Fig. 11, the lighter proton contributes less E<sub>5</sub> defects when compared with the He irradiation. Such a phenomenon is explained by the fact that the light projectiles, e.g. proton or electron, produce less complex defects e. g. interstitials and vacancies which subsequently neighbor with impurities and form vacancy-impurity complexes, meanwhile the divacancies are more probable to give birth under heavy ion irradiation 71. Moreover, as shown in Fig. 11, E<sub>1</sub> and E<sub>5</sub> both exhibit pronounced thermo-stability, presenting the possibility as majority carrier lifetime manipulator.

Table II Survey of deep level electron traps identified in proton and He irradiated silicon <sup>71,72</sup>.

Level	Bandgap position (eV)	Capture Cross section (cm <sup>2</sup> )	Identity
$E_1$	E <sub>C</sub> -0.167	$\sigma_n = 4 \times 10^{-15}$	$VO^{(-1/0)}+C_i-C_s^{(-1/0)}$
$E_2$	$E_{C}$ -0.213	$\sigma_{n}=1{ imes}10^{\text{-}14}$	? (H-related)
$E_3$	$E_{C}$ -0.252	$\sigma_{\rm n} = 7{ imes}10^{\text{-}15}$	$V_2^{=/-}$
$E_4$	$E_{C}$ -0.312	$\sigma_n = 4 \times 10^{-15}$	VO-H
$E_5$	$E_{C}$ -0.436	$\sigma_n = 3{\times}10^{\text{-}15}$	$V_2^{-/0}$
$E_6$	$E_{C}$ -0.463	$\sigma_{\rm n} = 2 \times 10^{-16}$	H-related (V <sub>2</sub> H)
E <sub>7</sub>	$E_{C}$ -0.507	$\sigma_n = 6 \times 10^{\text{-}17}$	? (H-related)

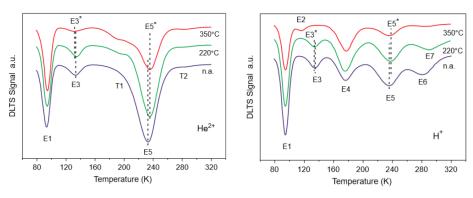


Figure 11 Majority carrier DLTS spectra of P+PN-N+ diode measured after (a) He+ irradiation and (b) H+

The exploration of tuning life-time in silicon *p-n* type device has been performed in the past decades. As shown in Fig. 12, when the irradiation project range is placed in different depth, e.g. the anode side of the junction inside (outside) of the space charge region, and the N base side of the junction, distinct contribution works on the lifetime of *p-n* device<sup>73</sup>. Due to the nature of produced electron traps, it is expected that when the projects range locates in the N base, an optimal manipulation would happen. Such an expectation was subsequently verified in many studies: As shown in Fig. 12, with both irradiation with proton and alpha particles, the measured reverse recovery waveforms of irradiated devices indicate that the sloping lifetime is obviously reduced by irradiation and furthermore results in the speed-up of the switch-off process <sup>67, 71-73</sup>.

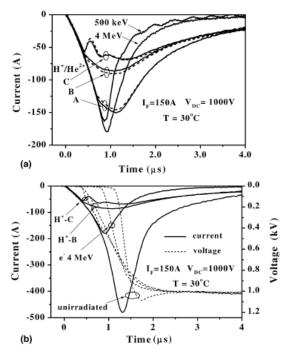


Figure 12 (a) Current reverse recovery characteristics of diodes irradiated by 500 keV ( $3 \times 10^{14}$  cm<sup>-2</sup>) and 4 MeV ( $2 \times 10^{13}$  cm<sup>-2</sup>) electrons (solid thin) and H<sup>+</sup>/He<sup>2+</sup> ions (fluence  $5 \times 10^{12}$  /  $5 \times 10^{11}$  cm<sup>-2</sup>, thick solid/dashed); (b) current (solid) and voltage (dashed) reverse recovery characteristics of the unirradiated diode and diodes irradiated by 4 MeV ( $2 \times 10^{13}$  cm<sup>-2</sup>) electrons and H<sup>+</sup> ions (fluence  $5 \times 10^{12}$  cm<sup>-2</sup>).<sup>73</sup>

However, the above-mentioned trade-off happened in SiC device is also inevitable in Si: The fast switch-off process is always accompanied with the sacrifice of forward voltage and current leakage. Of all generated defects, E<sub>5</sub> is always treated as the charging role who is responsible for the leakage, which is attributed to its location in the middle of the bandgap <sup>74</sup>. As a result, the irradiation with lighter ions, e. g. proton or electron, is preferred due to the less presence of E<sub>5</sub> defects to balance the trade-off between the dynamic benefit and static sacrifice. Afterwards, one started to explore the way of solving above-mentioned challenge by modifying the other function part in the device, e.g. the involve of novel electrode <sup>75-77</sup>. According to studies from J. Vobecky

et al., the replace of conventional aluminum or Ti-Ni-Ag electrode by platinum-silicide compound at the anode region outstandingly improves the drawback of raised leakage current and forward voltage. Actually, such a PtSi electrical contact could be achieved by a number of ways, e.g. the conventional platinum diffusion <sup>78</sup> or the proximity gettering <sup>79</sup>. As shown in Fig. 13, it is easy to note that according to the comparison between devices with PtSi+Al and Al+Al electrodes, the leakage current of device involved with PtSi contact was largely suppressed, which is even comparable with the value of un-irradiated device. Most importantly, the charge carrier life-time remains constant which means that the novel electrode does not negatively affect the dynamic properties. In addition to the reverse current, the drop of the forwards voltage is also partly cured by the involvement of PtSi anode electrode. As displayed in Fig. 14, the above-mentioned trade-off phenomenon is nicely elaborated by forward voltage drop versus turn-off losses in both low (1 A/cm<sup>2</sup>) and high (50 A/cm<sup>2</sup>) current density cases: upon increasing the irradiation energy, the turn-off loss reduces meanwhile the forward voltage drop increases. However, it is worth noting that by employing the PtSi anode, the drop of voltage remains constantly although the turn-off lose decreases till 2.2 and 10 mJ under the current densities of 1 A/cm<sup>2</sup> and 50 1 A/cm<sup>2</sup>, respectively. For the double Al anode samples, the voltage starts to dramatically raise at 4 and 80 mJ, respectively, which is two and eight times higher than the values of PtSi anodeequipped sample. By considering the absolute value of voltage drop, the compound anode also shows outstanding performance, in which the PtSi device irradiated under highest fluence presents similar voltage drop level (around 1.1 V in both low and high current density cases) as in unirradiated devices using Al electrodes, as shown in Fig. 14. Therefore, it is easily concluded that the employment of such novel anode would improve the static performance in SiC based devices.

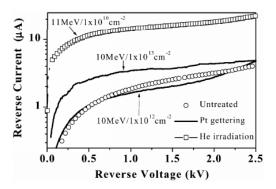


Figure 13 The reverse I–V curves measured at 30°C of the unirradiated and not annealed device (Untreated), the irradiated double Al electrode devices with He energy of 11 MeV and dose of  $1\times10^{10}$  cm<sup>-2</sup> (He irradiation), and the PtSi + Al electrode devices with He energy of 10 MeV and doses of  $1\times10^{12}$  cm<sup>-2</sup> and  $1\times10^{13}$  cm<sup>-2</sup>, both annealed at 700 °C for 20 min (Pt gettering) <sup>76</sup>.

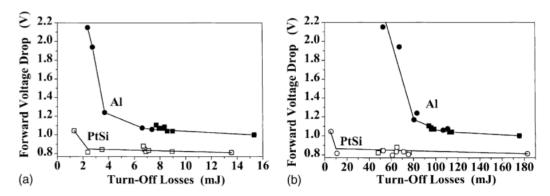


Figure 14 Trade-off between the ON-state voltage drop at 100 A and the turn-OFF losses measured at (a)  $V_{DC} = 500 \text{ V}$ ,  $J_F = 1 \text{ A/cm}^2$  and (b)  $J_F = 50 \text{ A/cm}^2$  for unirradiated and helium irradiated devices. For the devices with PtSi and Al anode contact layers the irradiation energies are 5.8 MeV (open squares) and 10 MeV (open circles) respectively 7.1 MeV (solid squares) and 11 MeV (solid circles)  $^{75}$ .

## **Summary**

In summary, the application of light ion (proton or alpha particle) or electron irradiation in modulating properties of both novel functional materials and PIN power devices has been systematically reviewed. By properly employing the irradiationinduced defects which generally act as carrier traps, it is possible to precisely tune the carrier concentration. Such compensation can be used to study/tune some properties which are determined by the carrier concentration, e.g. the Curie temperature, magnetization as well as uniaxial magnetic anisotropy in dilute ferromagnetic semiconductors or electrical-transport properties in topological materials. On the other hand, the compensation leads to the reduction of the carrier life-time which directly contributes to improving the dynamic performance of Si or SiC based PiN power devices, although several static performance parameters, including the forward voltage and current leakage, are somehow sacrificed. Nevertheless, such a trade-off has been well played to fulfill different application requirements. Considering the explosion of novel function materials and the energy revolution, it is believed that the light ion irradiation technique will do a great favor for both fundamental researches and industry applications.

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