Superinjection in diamond homojunction P-I-N diodes

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Abstract
Diamond and many newly emerged wide bandgap semiconductor materials show outstanding optical and magnetic properties. However, they cannot be as efficiently doped as silicon or gallium arsenide, which limits their practical applicability. Here, we theoretically predict a superinjection effect in diamond p-i-n diodes, which allows for the injection of orders of magnitude more electrons into the i-region of the diode than doping of the n-type injection layer allows. Moreover, we show that the efficiency of electron injection can be further improved using an i-p grating implemented in the i-region of the diode. The predicted superinjection effect enables us to overcome fundamental limitations related to the high activation energy of donors in diamond and provides the opportunity to design high-performance devices.

Keywords: superinjection, diamond diodes, light-emitting devices

1. Introduction
The operating principle of many semiconductor devices is based on the possibility of creating a high density of nonequilibrium carriers under a bias voltage. These carriers can further recombine or change the properties of the semiconductor which can, for example, be exploited for light modulation [1]. Light emitting devices, ranging from LEDs and lasers to single-photon sources, completely rely on this process [2–5]. In this regard, diamond, which has recently emerged as a material not only for high power electronics but also for room and high-temperature light emitting devices [5–11], is undoubtedly inferior to most semiconductors like gallium arsenide. The extremely high activation energy of donors (∼0.6 eV) [12] along with the non-zero donor compensation by acceptor-type defects limit the maximum density of free electrons in n-type diamond. Recent theoretical studies suggest that it may be possible to create shallow donors in diamond using a novel dopant [13], deuteration of boron-doped samples [14, 15] or codoping techniques [16–18], which provide the possibility of increasing the density of free electrons in n-type diamond. However, for various reasons, none of these doping techniques is in use for practical devices yet. At the same time, the maximum density of free electrons in the active region of homojunction optoelectronic devices is typically limited by the electron density in the n-type injection layer [19], which is typically as low as $10^{10}$–$10^{11}$ cm$^{-3}$ at room temperature [12, 20], regardless of the concentration of donor atoms. This doping problem does not give diamond-based devices the capability to compete with their more electron-rich semiconductor counterparts.

There are two possible strategies to overcome the electron density limitation. The first is extensive: by doping the n-type injection layer heavily with phosphorus, one creates a high density of hopping electrons [21–23]. These hopping carriers cannot be as efficiently used for recombination processes as electrons in the conduction band of diamond, but one can try to inject them into the undoped i-region of the p-i-n structure and

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partially convert these to conduction-band electrons. The second strategy is to create a smart structure that can inject a higher electron density than the n-type injection layer contains. Good examples of the application of such an intensive approach are heterostructure LEDs and lasers, where due to the potential barriers at the heterojunction, it is possible to accumulate high densities of non-equilibrium electrons and holes that can be orders of magnitude higher than the free carrier densities in the n-type and p-type injection layers. This phenomenon, known as superinjection [24, 25], was claimed to be a unique property of heterostructures which is not met in semiconductor homojunctions [26], i.e., it was believed that homojunction structures could not provide such a high level of electron injection. Recent papers on electron injection in homojunction diamond diode structures report that at doping densities of less than 10^{10} \text{ cm}^{-3}, the maximum injected electron density can be of the order of 10^{12} \text{ cm}^{-3} [5, 27]. However, such an electron injection efficiency is well below what could be achieved with heterostructures.

In this work, using a rigorous numerical approach, we predict for the first time the superinjection effect in homojunction diamond diodes. We show that in the i-region of the diamond p-i-n diode, it is possible to accumulate a density of free electrons higher than 10^{12} \text{ cm}^{-3}, which is nearly four orders of magnitude higher than the electron density in the n-type injection layer of the diode. Such an efficiency of electron injection is comparable with that provided by most heterostructures. In addition, we show that the injection efficiency can be further improved by implementing an i-p grating inside the i-region of the p-i-n diode. This approach offers the possibility of injecting a high density of electrons into a large volume. The enhanced efficiency of electron injection can be used to greatly increase the brightness of single-photon sources and light emitting diodes based on diamond.

2. Results and discussion

Figure 1 schematically shows the p-i-n and p-(i-p)\_x-i-n diamond diodes. The i-p grating of the latter can be used to achieve superior performance, which we will discuss below. The n-type region of the p-i-n diode is doped with phosphorus at a concentration of 10^{18} \text{cm}^{-3}. The donor compensation ratio by acceptor-type defects is 10%, which is typical for n-type diamond samples [28, 29] and provides a density of free electrons of \( n_{eq} = 6 \times 10^{10} \text{ cm}^{-3} \). The concentration of acceptors (boron) in the p-type region is equal to 10^{18} \text{ cm}^{-3}, and the acceptor compensation ratio is 1% [30]. The thickness of the i-region is selected to be 10 \text{mm} [20]. Such a thickness allows us to observe the superinjection effect at relatively low injection currents. Other parameters used in the numerical simulations are listed in table S1 which is available online at stacks.iop.org/SST/34/03LT03/mmedia. The p-i-n diode is simulated using the nextnano++ software (nextnano GmbH, Munich, Germany) [31], which is based on the self-consistent steady-state model (which comprises the Poisson equation for the electric field and carrier densities, semiconductor drift-diffusion equations for electrons and holes, and carrier continuity equations) and the finite difference method.

The results of the numerical simulations of the p-i-n diode are shown in figures 2 and 3. In equilibrium, there are no free carriers in the i-region. At forward bias voltages \( V \geq 4 \text{ V} \), electrons and holes are injected from the n-type and p-type regions, respectively. At \( V = 4.4 \text{ V} \) (\( J = 0.5 \text{ mA cm}^{-2} \)), the density of electrons in the i-region is as high as \( 2 \times 10^{10} \text{cm}^{-3} \) (figure 2)), but it is still lower than the electron density \( n_{eq} = 6 \times 10^{10} \text{ cm}^{-3} \) in the n-region, which is typical for semiconductor diodes [19, 32]. The grey line in figure 3 shows that at \( V = 4.6 \text{ V} \) (\( J = 0.1 \text{ A cm}^{-2} \)), the density of electrons at \( z = 1.9 \text{\mu m} \) exceeds \( n_{eq} = 6 \times 10^{10} \text{ cm}^{-3} \). The electron density in the i-region continues to increase as the bias further increases, and the position of the maximum in the electron distribution shifts towards the p-i junction. Figures 2 and 3 demonstrate that at high bias voltages, the maximum density of electrons in the i-region is orders of magnitude higher than the electron density in the n-region. This is what is known as the superinjection effect, which was previously predicted and observed only in semiconductor heterostructure [24, 25].

At bias voltages above \( \sim 4.6 \text{ V} \), the diamond p-i-n diode can be divided into two regions. In the first region (p-layer), the band bending (i.e., the electric field) is very weak compared with that in the second region (i- and n-layers), since the density of free carriers in the p-layer is much higher than in the i- and n-layers (see figure S2, stacks.iop.org/SST/34/03LT03/mmedia). Therefore, the diffusion electron transport dominates in the p-layer, i.e., the electron current can be expressed as \( J_{d} = qD_{n}\nabla n \approx qD_{n}E/L_{n} \), where \( q \) is the elementary charge, \( D_{n} \) is the electron diffusion coefficient and \( L_{n} \) is the electron diffusion length. At the same time, the drift electron transport dominates in the i- and n-layers, i.e., \( J_{o} = q\mu_{e}E_{0} \), where \( E \) is the electric field and \( \mu_{e} \) is the electron mobility. Since the recombination rate in the i-layer is relatively low due to the low density of defects, the electron currents at the p-i and i-n junctions should be of the same order of magnitude. At high bias voltages, the electric field in the n-layer is so high that the electron density in the p-layer near the p-i junction exceeds the electron density in the n-type layer. Additionally, the electron density gradient \( \nabla n = dn/dz \)
is positive at the p-i junction \( (z = 0) \), while the electron density in the n-layer is lower than in the p-layer under this high voltage condition. Therefore, a transition region with a high electron density, which exceeds the electron densities in both the n-type and p-type layers, exists in the i-type layer near the p-i junction to ensure current continuity. The formation of this transition region is inevitably accompanied by the formation of a potential well (see figures 2(b)-(d)) since the local increase in the electron density is accompanied by the local decrease in \( (E_c - F_n) \) and vice versa \( (E_c \) is the conduction band edge and \( F_n \) is the quasi-Fermi level for electrons). At high voltages, the electron density in the transition region can be as high as \( 10^{14} \) cm\(^{-3} \) (figure 3), while the density of free electrons in the n-type injection layer is only \( 6 \times 10^{10} \) cm\(^{-3} \).

We want to note that the superinjection can also be observed in conventional semiconductors, such as silicon, despite the fact that nobody has reported this effect yet. One can notice the high activation energies of donors and acceptors in diamond. Therefore, at low temperatures, the electron conductivity properties of silicon may be similar to that of diamond at room temperature. However, the efficiency of electron injection in silicon p-i-n diodes does not show a noticeable improvement as the device temperature decreases (see figure S3, stacks.iop.org/SST/34/03LT03/mmedia). As discussed in the above paragraph, the superinjection conditions can be achieved using the asymmetry in the mechanisms of electron conductivity at a high forward bias voltage: diffusion in the p-layer and drift in the i- and n-type layers. The only possibility to reach this in the silicon p-i-n diode is to reduce the doping level of the n-type injection layer to less than \( 10^{16} \) cm\(^{-3} \) while maintaining the same doping level \( (10^{18} \) cm\(^{-3} \) of the p-type layer. Figure S4 (stacks.iop.org/SST/34/03LT03/mmedia) shows that superinjection of electrons in the silicon p-i-n diode is possible even at room temperature. The strength of the effect is at least one order of magnitude lower than in the diamond diode of similar

![Figure 2](image_url)

**Figure 2.** (a) Energy band diagrams of the p-(i-p)\(_x\)i-n diodes \( (N = 0, 1, 2, 3, 6) \) at a forward bias voltage of 4.4 V. The thicknesses of the i-type and p-type regions of the i-p grating are equal to 400 nm and 200 nm, respectively, the grating period is 600 nm. The green area indicates the p-type injection layer. (b)-(d) The relative position of the conduction band edges of the p-(i-p)\(_x\)i-n diodes at bias voltages of 4.7 V (panel b), 8 V (panel c), and 13 V (panel d). (e)-(h) Electron density distribution in the p-(i-p)\(_x\)i-n diodes at four different bias voltages. (i)-(l) Hole density distribution in the p-(i-p)\(_x\)i-n diodes at four different bias voltages. The I-V characteristics of the p-(i-p)\(_x\)i-n diodes can be found in supplementary material. (stacks.iop.org/SST/34/03LT03/mmedia)

![Figure 3](image_url)

**Figure 3.** Dependence of the electron density on the injection current at four different points in the i-region of the p-i-n diode shown in figure 1(a). The orange line shows the maximum electron density that can be created in the i-region of the diode, and the grey line shows the position of this maximum.

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dimensions. However, the main problem in this case is that the superinjection effect does not provide any practical benefits since a higher density of injected carriers can be achieved simply by increasing the doping level to $N_d = 10^{18} \text{ cm}^{-3}$. The situation is different for diamond, where the required asymmetry in the mechanism of electron conductivity is naturally provided by the extremely high activation energy of donors even at high doping levels ($\sim 10^{18} \text{ cm}^{-3}$) in both the p-type and n-type injection layers, which ensures strong superinjection at room and even higher temperatures and allows for the injection of nearly four orders of magnitude more electrons than the doping of the n-type injection layer provides.

Can one further improve the efficiency of electron injection in the diamond p-i-n diode? Figures 2(g), (h) and 3 show that at high injection levels, the width of the region with a high electron density is as low as 300–500 nm, while the remaining volume of the 10-μm-thick i-region is not used efficiently. Moreover, the width of the region with a high electron density only decreases as the bias voltage increases. One of the possibilities to overcome this problem is to use a double heterostructure, which allows for the creation of a wide potential well for electrons, as is done in III–V semiconductor light emitting devices [2, 3, 24, 25]. However, in the case of diamond, we do not have any compound semiconductors that are lattice matched to diamond with a narrower or wider bandgap perfectly aligned with respect to the conduction band of diamond.

We propose to use an i-p grating implemented in the i-region of the p-i-n diode (figure 1(b)). By selectively doping the i-region, we can artificially control the band bending in the i-region near the p-i junction at high voltages and create potential wells for electrons (figures 2(c), (d)), where it is possible to efficiently accumulate a high density of electrons at voltages above 7 V (figures 2(g), (h)). Figures 2(e)–(g) clearly shows that a single 600-nm-thick i-p insert (which consists of the 400-nm-thick i-type layer and the 200-nm-thick p-type layer) in the i-region of the p-i-n diode does not affect the electron distribution in the remaining i-region of the p-i-n diode at moderately high bias voltages. Therefore, this i-p insert additively contributes to the injection efficiency without deteriorating the superinjection effect in the remaining i-region. It is remarkable that even a thick i-p grating with six periods of 600 nm does not change the maximum electron density (figures 2(f), (g)) and only slightly reduces the width of the area with a high electron density in the remaining i-region due to the decreased thickness of the remaining i-region and increased influence of the i-n junction on the electron distribution in the i-region [20, 33]. At the same time, electrons are efficiently injected into the i-p grating creating a wide region with a high electron density (figures 2(f), (g)), which can be efficiently exploited in the design of light emitting devices.

At bias voltages above 11 V (figures 2(d), (h), (l)), the influence of the i-p grating on the remaining i-region is stronger. However, we should note that such regimes are less favorable for light emitting devices due to the much higher currents and slightly lower electron densities (figure 2(g)).}

Nevertheless, the i-p grating can significantly improve the diode characteristics in these regimes. Figure 2(g) shows that at bias voltages above 11 V, the six-period grating slightly decreases the maximum density of electrons in the i-region. However, the total number of injected electrons between the n-type and p-type injection layers of the diode is 25% higher than in the p-i-n diode without the grating and the width of the region with a high electron density is 5 times larger.

It is important that at moderately high bias voltages ($V < 11$ V), the electron density in each cell of the i-p grating is absolutely the same in spite of the large length of the i-p grating and the relatively strong electric field in the i-region (figures 2(f), (g)). Color centers created in the i-type inserts of
the i-p grating would demonstrate absolutely the same emission rates and other properties (see figure 4), which can be beneficial for the design of reproducible electrically pumped single-photon sources or light emitting diodes based on color centers in diamond.

Another important advantage of the implementation of the i-p grating is the greatly improved hole injection efficiency, which is clearly seen in figures 2(i)–(l). The i-p grating allows for the accumulation of holes across the whole i-p grating. The maximum density of holes in the p-type inserts of the grating is as high as in the p-type injection layer, while the hole density in the i-type inserts is only four times lower. The improved hole injection efficiency can greatly increase the number of free excitons (see figure 5), especially at high forward bias voltages (figure 5(b)), since the exciton density is determined equally by both the electron and hole densities [37].

3. Conclusions

In summary, we have numerically demonstrated that although the high activation energy of donors in diamond limits the density of free electrons in the n-type injection layer to only $10^{10} - 10^{11}$ cm$^{-3}$, it is possible to inject nearly four orders of magnitude more carriers into the i-region of the p-i-n diamond diode. Moreover, we have shown that the electron injection efficiency can be further improved using an i-p grating implemented in the i-region near the p-i junction. Until recently, it was believed that the superinjection effect was a distinct feature of semiconductor heterostructures [24, 26] and could not be observed in p-n and p-i-n homojunctions. However, we have shown that superinjection conditions can be produced in diamond homojunction structures at room and even higher temperatures. Such structures that exploit the superinjection effect open new opportunities in the design and engineering of high-performance optoelectronic devices based on diamond and other wide-bandgap semiconductors.

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