Silicon carbide has been widely used as material for manufacturing yellow, red, green LED and optoelectronics devices (indicators, screens). The silicon carbide LED technology has been investigated for improvement of their operational characteristics. This includes the influences of the surface processing (etching, annealing), the formation method for the p-n junctions and the contacts on the LED properties. Light-emitting devices used as light sources for optical-fiber communication lines. LED fabricated by Al⁺ ion-implanted in 6H-SiC and investigated their characteristics for an effective green LED. The brightness of the ion-implanted p-n junction was found to be two orders higher than that of diffusion p-n junction, and the best value was 2000-10000 cd/m² with passing current about 0.5mA through area 50x50 µm and applied voltage about 2.6±0.2V. The ion-implanted structures showed a high stability of light in the temperature range of 77-600K.

Keywords: Silicon carbide, LED, Ion implantation

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1. Introduction

Silicon carbide LED first became a significant commercial success when NREE (USA) got them on the market in the early 1990’s. Today, CREE’s CB series of super bright LED are a new generation of solid-state LED emitters, which combine highly efficient InGaN with CREE’s SiC substrate. CREE’s main LED products now have SiC as a substrate for gallium nitride or indium gallium nitride as active ingredients, and emit blue as well as green and blue-green luminescence. Yellow silicon carbide LED’s had been made around 1970-1975 in the former Soviet Union. Diffusion p-n junctions had been applied to manufacturing this LED devices. Single crystalline SiC with Np×Nn=(1~5)×10¹⁷ cm⁻³ was suitable for manufacturing such devices. The diffusion factors depend on the concentrations of the impurities in the crystals. The process of p-n junction creation is rather complicated because the usual impurity concentrations in crystals range from 10¹⁷ to 10¹⁸ cm⁻³. The optimal depth (1µm) of the p-n junction had been obtained with industrial crystals [1].

To obtain a high manufacturing yield for LED with uniform light, the following technique had been applied. Diffusion of Al with O was carried out for 2 hr at 1700°C. Then, B and Al were introduced for 15 min at 1600°C. The sources for O, Al, and B were SiO, 99.99% Al and B₂O₃, respectively. After the diffusion processes, appreciable changes in the surface morphology or the carbon traces were observed using optical microscopy. The low-temperature (77K) and the high-temperature (300K) photoluminescence in the ultraviolet wavelength range showed repeatable and clear spectra for the uniformly doped samples. Diffusion of Al and O above 1700°C resulted in a deterioratıon of the surface conditions, and diffusion of B and Al at higher temperatures made the photoluminescence spectra less clear and the surface conditions even worse. The time at optimum temperature could be adjusted to change the color of electro-luminescence from yellow-green to red (in the wavelength range between 5600Å and 6000Å). In the case of a yellow-green color (5600Å), the time for the diffusion of B and Al turned out to be 20-25min. A further increase in the diffusion time caused the p-n junction to be less sharp as well as the voltage drop on the p-layer to increase, and, consequently, spreading of the current carriers on the p-layer and less clear light drawings on the displays. At the shortest diffusion time (5min) for B and Al, the thickness of the p-n junction was too small to assure an effective LED. The parameters of such LED and indicators, which had been fabricated, are listed in Table 1. Usage of another SiC polytypes (4H, 3C, 15R) allows to change the color of light, too.

Because of the extreme stability of silicon carbide, it is not necessary to dope the crystal by thermal diffusion. Instead, dopants can be introduced by ion implantation. Once implanted into the crystal, the dopant atoms occupy interstitial positions in the lattice and must be transferred to substitution sites to become electrically active. This “activation” is accomplished by high temperature annealing in an inert ambient such as argon. Nitrogen and phosphorous are typical n-type dopants in SiC.
### Table (1) LED (diffusion p-n junction) on 6H-SiC

<table>
<thead>
<tr>
<th>Device</th>
<th>Light voltage (V)</th>
<th>Light current (mA)</th>
<th>Working voltage (V)</th>
<th>Brightness (cd/m²)</th>
<th>Size of light area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LED indicator (10 elements)</td>
<td>2.2</td>
<td>5</td>
<td>2.4±0.2</td>
<td>30-80</td>
<td>800x300 step 100</td>
</tr>
<tr>
<td>LED matrix (64 elements)</td>
<td>2.5±0.1</td>
<td>0.5</td>
<td>3.0±0.2</td>
<td>60</td>
<td>120x120 step 100</td>
</tr>
<tr>
<td>LED break with high resolution (64 elements)</td>
<td>2.4±0.2</td>
<td>2.5</td>
<td>3.1±0.1</td>
<td>70</td>
<td>40x40 step 60</td>
</tr>
<tr>
<td>LED break (100 elements)</td>
<td>2.4±0.2</td>
<td>0.5</td>
<td>2.8±0.1</td>
<td>80</td>
<td>100x100 step 100</td>
</tr>
<tr>
<td>LED break with face conclusion of light (step 100)</td>
<td>40x40 step 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Aluminum and boron are p-type dopants. Implantation is usually conducted with the sample at elevated temperatures (600-800°C) to provide some in-situ annealing of lattice damages caused by the implant. The implanted sample is subsequently annealed at temperatures 1000-1700°C for times 5 and 90 minutes to activate the dopants. The dynamics of activation depends both on the dopant species (i.e. aluminum and boron, nitrogen and phosphorus) and upon the SiC polytype (i.e., 4H or 6H). Activation of nitrogen implants in 4H-SiC requires higher annealing temperatures than those in 6H-SiC. Phosphorus is an excellent n-type dopant in 4H-SiC when implanted at high doses, such as for source and drain regions of MOSFET p-type dopants, aluminium and boron, require much higher temperatures for efficient activation and temperatures above of 1650°C are necessary for that. Aluminum implants typically achieve the same degree of activation at annealing temperatures about 100°C lower than boron. At any given annealing temperature, there exists an optimum annealing time.

This article reports results of SiC green LED electrical characterization. This LED had the same brightness as CREE’s LED, but higher stability, more simple design (without AlGaN or GaN layers) and can be used in various usual applications.

#### 2. Experiment

Green LED had been prepared by the method of ion implantation of impurities into 6H-SiC crystals. Al⁺-implanted for p-n junctions in 6H-SiC substrates and their characteristics were investigated as an effective LED. The ion-implantation was carried out on polished n-type 6HSiC crystals and on epitaxial layers of 6H-SiC with an impurity concentration of \( N_p x N_n = (2-8)\times10^{18} \) cm⁻³. Substrate was doped by donor nitrogen. Implantation was performed with 80keV Al⁺ by using an ion accelerator. The implanted depth was 0.5µm, and the concentration of Al was \( 10^{20} \) cm⁻³. The optimum implantation time and the substrate temperature were 2 min and 660°C, respectively.

Despite the low resistance of the p-layers, a thin high resistive layer of C was formed on the surface of the crystals after implantation. This C film reduced the adhesion of the metals deposited for the contacts, increased the resistance of the contacts to the p-layers, and worsened the light uniformity. The crystals were annealed at 800-1100°C for 2-10 min to remove the C layer and to reduce the quantities of radioactive defects. Before the LED fabrication process, the crystals were etched in an acid mixture of HF and HNO₃.

Contacts were prepared by deposition of Al layer on p-SiC heated to the temperature 550°C in vacuum (implanted and annealed). Al contact thickness was less or about 4000Å. Ni layers was deposited for protection of Al layer from oxidation and for better contact with wire during LED manufacturing. Thickness of Ni layer was about 2000Å. Contacts to the n-SiC substrate were made by laser using Ti and Ni wire. Contact of necessary configuration were made by photolithography methods.

#### 3. Results and Discussion

Photos of prepared LED are shown in Fig.1 (a, b, c). Just this LED was made on n-epitaxial layer grown by Tairov’s method. The boundary between n-layer and implanted p-layer is shown. The block structure of epilayer and p-n junction is also shown. Single crystals grown by the Lely method had been used for such LEDs, too, but photos of epilayers with implanted aluminum are more interesting than these of single crystals with p-n junction. The voltage-current characteristics of ion-implanted p-n junctions are shown in Fig. 2. The differential degree \( \alpha = d\ln I / dV \) is shown in Fig. 3.

In the low voltage area (at a voltages less then 0.08V), \( \alpha \) is about unity. Determined from this linear site leakage is \( (1-2)\times10^5 \)Ω. The reason of such resistance is carbon or silicon oxide on the surface of LED. In the region of very small voltages:

\[
I = I_0 \exp \left( \frac{V}{VT} \right) \tag{1}
\]

This circumstance, as well as independence of \( V_T \) on temperature permits to think about tunnel character of this part of the voltage-current characteristics. Concentration evaluated from a volume charge is as follows:
\[ N = \frac{1}{e} \int_{\frac{n}{e}}^{e} \frac{\rho(n)}{n} dn = \frac{\pi^2 e m}{32 h^2} V_T^2 \]  

\[ N \approx (1-4) \times 10^{20} \text{cm}^{-3} \text{ is indicative of a rather high doping level of the junction. The ideality factor 1.9 to 3.2 was obtained from the following exponential part of the forward bias current-voltage characteristics. The forward saturation current was (3-5) \times 10^{-10} \text{ to } (3-5) \times 10^{-8} \text{ A/cm}^2 \text{ and forward turn-on voltage of 0.8 to 2V (at current density about (5-8) \times 10^{-8} \text{ A/cm}^2. Reverse biasing produced average leakage currents were that were of the order of } 10^{-8} \text{ to } 10^{-3} \text{ A/cm}^2 \text{ (at 10 to 20V reverse bias).}

The ideality factor had some trends. Namely, the ideality factor is decreased and forward current density is increased with increasing operation temperature in the range of 20°C to 400°C. The ideality factor is of the order of 2 for most LED suggesting that recombination/generation current is dominant over diffusion current. The ion-implanted p-n junctions are sharp, and the injection of carriers as well as their recombination in the player prevail. The sharpness was maintained in the temperature range between 77K and 500K. Recombination happens in the layer of the volume charge in the p-n junction at low levels of injection, but the recombination prevails in either the p- or the n-area at high levels of injection, depending on the doping degree.

\[ V = \begin{cases} \frac{2}{B} I_0^2 + V_0 \\ \frac{2}{B} I_0^2 + V_{\infty} \end{cases} \]  

In the region of voltages changing from 2.2V to 18V the \( \alpha \) degree is reduced passing the flat minimum. Then \( \alpha \) degree (Figs 2, 3) is again increased and can be described by the expression:

\[ \tau_n = \frac{L^2}{2 \mu V_0} = (0.8 - 1.2) \times 10^{-8} \text{ s} \]  

(a)  

(b)  

(c)  

Fig. (1): Micro photo of ion-implanted LED: Magnitude, (a) \times 75, (b) \times 380, (c) \times 730  

Fig. (2): Voltage-current characteristics of ion-implanted p-n junction in 6H-SiC  

Fig. (3): Derivation from voltage-current characteristics of ion-implanted LED
That is in good agreement with the experimental data of transitive characteristics, where ignition time is \((2.5-3) \times 10^{-8}\) s and emission time is \((1-1.5) \times 10^{-8}\) s. The light-brightness characteristic of the ion-implanted p-n junction is shown in Fig. 4. The differential degree \(\beta = dB/d\lg I\) is shown in Fig. 5. The linear region extends from \(7 \times 10^{-4}\) A to \(10^{-2}\) A/cm². The high stability of the light, even at 77-600K, is another characteristic for the ion-implanted structures, which is understood mainly by the role of the radioactive defects in the emission. The concentration of defects is constant in the temperature range of 77-600K.

Fig. (4): Ion-implanted p-n junction light brightness characteristics

The destructive features of the ion-implanted structures produced narrow lines in the electroluminescence spectra at relatively small current (Fig. 6). A correlation between the narrow lines in the spectra and the brightness of LED had been established; most of the effective LED had narrow lines at low temperatures. It is a very convenient way to select crystals for green highly bright LED. When the temperature increases, the narrow lines disappear from the spectra. The fact that the sharp-line structures of the electroluminescence spectra coincide with those of the photoluminescence spectra at low temperatures (77K) is an additional indication to support the suggestion that the characteristics of the spectra are due to radioactive defects.

Fig. (5): Derivation from brightness-current characteristics of ion-implanted p-n junction

Fig. (6): Ion-implanted p-n junction electroluminescence spectrum

The ion-implanted structures have much faster response times than the diffused ones (Table 2). The switching time is close to \(10^{-8}\) s, which provides wide opportunities for the applications of such LED to optical couples and optical-fiber communication lines. The brightness of the diffused LED is 30-100 cd/m² at 10mA/mm², while for the ion-implanted it is 500-600 cd/m² at 10mA/mm² and even (2-10)1000 cd/m² for the best samples. On the other hand, ion-implanted p-n junctions can be applied widely in optical-fiber communication, especially, short communication lines, because of their high speed (\(10^{7}\) s), high stability of light for 10,000 hrs, linear brightness-current characteristics up to a current density of \(10\) A/cm², high brightness, absence of brightness degradation, and stability of characteristics over a wide interval of temperatures.

**Table (2)** LED for the fiber communication line

<table>
<thead>
<tr>
<th>Switching voltage (V)</th>
<th>Switching current (mA)</th>
<th>Working voltage (V)</th>
<th>Brightness (cd/m²)</th>
<th>Size of light area (μm²)</th>
<th>Switching time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6±0.2</td>
<td>0.5</td>
<td>3.2±0.1</td>
<td>2000-4000</td>
<td>50x50</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80x50</td>
<td></td>
</tr>
</tbody>
</table>

Characteristics of p-n Junction Silicon Carbide LED
4. Conclusion
The characteristics of silicon carbide LEDs were investigated. These included the influence of surface processing, the formation method of the p-n junctions, and the contacts on the properties of the LED. Green SiC LEDs can be used as light sources for optical-fiber communication lines, in the traffic lights, as indicators, in screens and so on. p-n junctions were fabricated by Al⁺ ion-implantation 6H-SiC, and annealed at 800-1100°C. Characteristics for using as effective green LED had been investigated. The brightness of the best ion-implanted p-n junction was found to be about 2000-10000 cd/m². The ion-implanted structures showed a high stability of light in the temperature range of 77-600K. The pulsing characteristics of these LEDs based on ion-implanted structures had a response time close to 10⁻⁸s.

References

This article was reviewed at The Department of Electrical and Computer Engineering, National Technical University of Athens, Greece

The 5th International Conference on Atomic and Molecular Data and Their Applications (ICAMDATA)
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We cordially invite you to attend the Fifth International Conference on Atomic and Molecular Data and Their Applications (ICAMDATA) that will be held October 15-19, 2006 in Meudon, France at the observatory of Paris. Topics covered by the conference include atomic and molecular data production, collection, assessment, and dissemination, laboratory data needs and applications, astrophysical and atmospheric applications, inertial and magnetic fusion, lighting, plasma processing, and other similar applications relying on understanding of atomic and molecular processes and needing atomic and molecular data.

Deadline for abstract submission : September 17th