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(72) Inventor IZUO HAYASHI

(54) IMPROVEMENTS IN OR RELATING TO LIGHT EMITTING SEMICONDUCTOR DEVICES

(71) We, WESTERN ELECTRIC
 COMPANY, INCORPORATED, of 195
 Broadway, New York City, New York
 State, United States of America, a
 Corporation organized and existing under
 the laws of the State of New York, United
 States of America, do hereby declare the
 invention, for which we pray that a patent
 may be granted to us, and the method by
 which it is to be performed, to be particu-
 larly described in and by the following
 statement:—

The invention relates to light emitting
 semiconductor devices, including both semi-
 conductor injection lasers and electro-
 luminescent diodes.

In 1962, R. N. Hall et al reported in
 Physical Review Letters 9, 366, their observa-
 tion of coherent light emission produced by
 electron-hole recombination in GaAs p-n
 junctions. Typically, GaAs lasers are fabri-
 cated by diffusing zinc into n-type GaAs
 wafers with donor concentrations in the order
 of $10^{18}/\text{cm}^3$. For structural details, see
 Masers and Lasers, Thorp, J.S., Chapter 10,
 St. Martin's Press, New York (1967).
 Injection lasers have also been constructed
 from other semiconductors, e.g., InP, InAs
 and InSb. All such lasers, however, are
 fabricated from one kind of semiconductor
 material in which the band gaps are equal on
 either side of the junction. The semicon-
 ductor is usually monocrystalline. In the
 semiconductor junction laser coherent radia-
 tion results from electron transitions between
 broad energy bands, i.e., between the con-
 duction and valence bands. These junctions,
 and in particular GaAs junctions, are pumped

mainly by the injection of electrons into the
 p-side of the junction by the direct applica-
 tion of an electrical current. The injection
 process produces a population inversion
 between a pair of electron energy levels when
 pumped at a sufficiently rapid rate and with
 sufficient power input. In semiconductor
 lasers this power threshold may be as high
 as 10^8 to 10^9 watts/cm² (or 10^5 watts/cm²)
 at room temperature, whereas by comparison
 in gas or crystal lasers the pumping power
 needed is usually in the range of 1 to 1000
 watts/cm². Obviously, the enormous power
 requirements of such semiconductor lasers at
 room temperature cannot be maintained very
 long without damaging the semiconductor.

It is known, however, that the power (or
 equivalently the current density) threshold in
 most prior art devices is approximately pro-
 portional to the cube of the absolute tem-
 perature in the temperature range near room
 temperature. Consequently, semiconductor
 lasers generally are operated more easily in
 low temperature environments. For example,
 GaAs lasers have been operated at liquid
 nitrogen temperatures (77°K) with a thresh-
 old of about 1000 amperes/cm². To date
 the highest temperature CW operation
 reported appears to have been achieved by
 J. C. Dymant and L. A. D'Asaro et al at
 200°K as reported in Applied Physics
 Letters 11, 292 (1967).

The invention provides a light emitting
 semiconductor device comprising semicon-
 ductive regions of first and second con-
 ductivity types having wide band gap and,
 interposed therebetween a first common con-
 ductivity type heterojunction and a second

[Price 25p]

common conductivity type heterojunction spaced from the first heterojunction, the distance between the heterojunctions defining an intermediate region containing a p-n junction and having a narrower band gap region than the regions adjacent the other sides of the heterojunctions, the p-n junction being separated from the first heterojunction by a distance less than a diffusion length of minority carriers injected towards the first heterojunction and the p-n junction being spaced from the second heterojunction by a distance less than a diffusion length of minority carriers injected towards said second heterojunction and adapted so that the application of operating energy to the device provides a forward bias across the p-n junction to inject minority carriers across the p-n junction and produce radiative recombination of holes and electrons.

As used herein, a "heterojunction" is defined as the interface between contiguous layers having different band gaps and is further defined as p-p, n-n or p-n (or n-p) depending on the majority carrier type on either side of the interface. The p-n and n-n types will hereinafter be referred to as "common conductivity type heterojunctions." Moreover, it is to be understood that a "p-n junction" includes either a p-n heterojunction or a p-n homojunction. In the homojunction the band gaps on either side of the junction are equal.

When provided with an appropriate optical resonator and when forward biased, the light emitting semiconductor device exhibits lasing at lower thresholds and higher temperatures than heretofore possible, radiative recombination occurring between the conduction and valence bands. This result is believed to be due primarily to an electrical confinement effect produced by an energy step in the band structure which confines injected minority carriers to the intermediate region. To take advantage of this confinement it is important that the thickness of the intermediate region (defined, as above, to be the distance between the appropriate junctions) be less than the diffusion length of minority carriers. As the thickness of a single heterojunction diode (SH) is reduced confinement increases and the threshold decreases until a point where the onset of hole injection (out of the intermediate region) occurs. Thereafter the threshold begins to increase. Hole injection can be reduced by making the band gap of the region adjacent the p-n junction greater than that of the intermediate region. In the SH diode this may be accomplished by appropriate doping. In a double heterojunction diode (DH), however, this is effectively accomplished by fabricating the diode as a three layered structure in which the intermediate narrow band gap layer (e.g., p-Al_xGa_{1-x}As) is sandwiched between a pair of wider band

layers, (e.g., n-Al_xGa_{1-x}As, p-Al_yGa_{1-y}As, where $y < x$ and $y < z$). Illustratively, $y = 0$ and the intermediate region consists, therefore, of p-GaAs. The DH, therefore, includes an n-n heterojunction, an n-p homojunction and a p-p heterojunction in which the first two junctions are separated by a distance d_1 less than the diffusion length of holes D_H and the second two junctions are separated by a distance d_2 less than the diffusion length of electrons D_E . Moreover, the separation of the two heterojunctions (i.e., the thickness t of the intermediate region) should be greater than about one-half wavelength of the radiation as measured in the intermediate region (e.g., $\lambda = 0.25\mu$ in GaAs). That is, the following relationships should be satisfied:

$$d_1 \leq D_H \quad (1)$$

$$d_2 \leq D_E \quad (2)$$

$$\frac{\lambda}{2} < t \quad (3) \quad 85$$

It should be noted that the p-n junction may be coincident with either heterojunctions. Where the n-n heterojunction and n-p homojunction are coincident to form an n-p heterojunction, then $\lambda/2 < t < D_E$. Similarly,

where the p-n heterojunction and the n-p heterojunction are coincident to form an n-p heterojunction, then $\lambda/2 < t < D_H$.

The conditions of equations (1) and (2) which limit the maximum thickness of the intermediate region, arise from the fact that for carrier confinement to exist the carriers must be able to reach the heterojunction, there to be repelled by the electric field produced by the energy step in the band structure. On the other hand, condition (3), which limits the minimum thickness of the intermediate region, is somewhat more complicated and is related to the amount of leakage optical field (i.e., field outside the intermediate region which acts as a waveguide) which can be tolerated. An excessive amount of such leakage increases optical absorption losses and decreases the coupling between radiation and recombination (i.e., decreases stimulated emission), both of which increase the lasing threshold. Calculations based upon the teachings of D. F. Nelson et al in Journal of Applied Physics, 38, 4057 (1967) indicate that $\lambda/2$ sets an approximate lower limit. In GaAs and mixed crystals thereof $\lambda/2 \approx 0.125\mu$.

Additional reduction in the lasing threshold occurs, as described in British Patent Application No. 49780/69 (Serial No. 1288082), if deep impurity levels or deep band tails near the valence band are provided

in the intermediate region (on either or both sides of the p-n junction) in which case lasing is achieved by electron-hole recombination between the conduction band and the deep levels. Still further improvement in the temperature coefficient of threshold may be achieved by providing deep band tails near the conduction band in addition to the deep levels provided near the valence band. In an exemplary embodiment, the pair of semi-conductive layers utilised are GaAs and a mixed crystal of $p\text{-Al}_x\text{Ga}_{1-x}\text{As}$ or $p\text{-GaAs}_{1-x}\text{P}_x$ in which the band gap in the mixed crystal is the greater.

Without an optical resonator, both the SH and DH diodes when forward biased function as electroluminescent diodes, incoherent radiation being emitted from the intermediate region through the wide band gap region, thereby resulting in lower absorption losses and high efficiency. Dome-like configurations of the wide band gap region further increase efficiency by reducing reflection losses at the interface between the wide band gap region and the external atmosphere.

The invention, together with its various features and advantages, can be more easily understood from the following more detailed description of embodiments taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic of one illustrative embodiment of a laser not *per se* forming part of the invention;

Fig. 2 is a schematic of an electroluminescent diode;

Figs. 3 and 4 are schematic diagrams showing the relative positions of the homo-junctions and heterojunctions.

Turning now to Fig. 1, there is shown an illustrative embodiment in which a semiconductor single heterostructure (SH) injection laser 10 comprises wide and narrow band gap layers 12 and 14, respectively, fabricated from different semiconductor materials disposed upon a heat-sink 16. A current source 18 is connected across the structure via electrodes 20 and 22 deposited, respectively, on the upper surface of the layer 12 and between heat-sink 16 and layer 14. An intermediate region 24 is defined as the region between p-p heterojunction 23 and p-n homo-junction 25, the latter being located in the narrow band gap layer 14. When the device is forward biased and pumped by source 18, it emits coherent radiation 26 in the plane of the region 24 as shown. The two opposite surfaces 28 and 30 which are perpendicular to the plane of the intermediate region 24 are polished or cleaved flat and parallel by techniques well known in the art to within a few wavelengths of the coherent radiation to form a plane parallel optical resonator. The other pair of surfaces 32 and 34 perpendicular to the region 24 are often roughened.

A reflective coating on the polished surfaces 28, 30 or a structure which has four polished sides, may be utilised in order to enhance the Q of the optical cavity.

As pointed out previously, one feature of this embodiment is that the injection laser has a diode structure which exhibits a confinement effect as described in British Patent Application No. 49780/69 (Serial No. 1288082). It has been found further that an intermediate region thickness (i.e., t) of about 2.0μ is preferred. A larger t reduces the confinement effect and thereby increases the threshold. In a structure without the aforementioned difference in effective band gaps between the narrow band gap and intermediate regions, a much smaller t results in the onset of hole injection and hence also increases the threshold.

The SH diode comprises a pair of contiguous semiconductive layers having different band gaps with a p-n junction located in the narrow band gap region and separated from a p-p heterojunction, located at the interface between the layers, by a distance d_1 less than the diffusion length D of minority (i.e., injected) carries at the operating temperature of the device. Typically, the diffusion length is about 1μ , but, depending on the doping levels and other parameters, could be larger.

The separated p-n junction and p-p heterojunction thus define three regions of interest: a narrow band gap region of one conductivity type, an intermediate region, and a wide band gap region of a second conductivity type. The narrow band gap typically is of the order of 5—6 mils, but to enhance the removal of heat from the device the narrow band gap region can be considerably thinner e.g., <0.2 mils. The intermediate region may have an effective band gap equal to, or slightly less than, that of the narrow band gap region, and generally is of the same conductivity type as the wide band gap region although it may be less heavily doped than the wide gap region.

A distinction will be made hereinafter between the band gap and the effective band gap of a semiconductor. The band gap is defined as the energy difference between the minimum energy in the conduction band and the maximum energy in the valence band in an undoped semiconductor.

In the presence of a sufficiently high density of either donor or acceptor impurities, however, band tails exist on both the conduction and valence bands. Consequently, the energy distribution is an asymptotic function and therefore the aforementioned minimum and maximum are not clearly defined. An effective band gap will therefore be defined as follows. Find the energy level near (just below) the bottom of the conduction band such that just as many of the introduced

donor states lie above as lie below that level. Find a similar level near the top of the valence band. The difference between these two levels is termed the "effective band gap".

5. In the following discussion, it will be assumed for the purpose of illustration that the conductivity type of the narrow band gap, intermediate, and wide band gap regions is n-p-p, respectively. The effective band gap of each of these regions will be designated E_{gn} , E_{gi} , and E_{gp} , respectively.

10. It is possible, of course, to fabricate a diode by utilising contiguous mixed crystal layers, e.g., a wide band gap $Al_xGa_{1-x}As$ layer and a narrow band gap $Al_yGa_{1-y}As$ layer in which $0 \leq y < x$.

15. As discussed with reference to the SH diode, but for the onset of hole injection which causes holes to be lost for radiative recombination purposes, it would be desirable to decrease further the thickness of the intermediate region. While the aforementioned difference in effective band gap between the narrow band gap and intermediate regions reduces such hole injection, it has been found that the double heterostructure diode increases significantly the confinement of both holes and electrons between the two heterojunctions, thereby
20. resulting in lasing at a lower threshold at room temperature than even the SH diode.

- The DH diode, shown in Fig. 3 with the dimensions exaggerated for the purposes of illustration, comprises in one embodiment a heat-sink 216 on which is formed a multi-layered structure including a metal contact 219, a substrate 214, a wide band gap n-type layer 215, a narrow band gap region 224, a wide band gap p-type layer 212, a contact layer 217 and a second contact 218. It should be noted that it is readily possible to fabricate the heat sink on contact 218, or on both contacts 218 and 219.

- A p-p heterojunction 223 is located at interface between layer 212 and region 224 whereas an n-n heterojunction 225 is located at the interface between region 224 and layer 215. In addition, a p-n homojunction 226 is located between the heterojunction at a position such that equations (1)–(3) are satisfied. Alternatively, the p-n junction 226 may be coincident with n-n heterojunction 225 in which case they form a p-n heterojunction 222 as shown in Fig. 4 (i.e., $d_2=0$, $d_1=t$).

55. When a DH diode is provided with an appropriate optical resonator and forward biased, both by means well known in the art, electrons injected across the p-n homojunction 226 are reflected by p-p heterojunction 223 and undergo radiative recombination. And, whereas holes also undergo injection in the opposite direction across p-n homojunction 226, they are reflected by n-n heterojunction 225 and also undergo recombination.
65. Thus, both injected holes and electrons are

electrically confined to the intermediate region 224 resulting in lower thresholds at room temperature than heretofore possible, provided, of course, that the criteria defined by equations (1)–(3) are met. Preferably, $0.125\mu < t < 1\mu$ (e.g., $t=0.8\mu$) for a GaAs

intermediate region. It should be noted that optical confinement produced by the two heterojunctions (which form a waveguide) also contributes somewhat to lower thresholds.

An example describing the manufacture of a double heterostructure will now be given. Briefly, the apparatus utilised in the manufacture includes a seed holder and a solution holder having a plurality of wells and adapted to be slid into position over the seed. The assembly was placed in a growth tube and inserted in a furnace (of the type not having a window port).

A silicon doped gallium arsenide wafer (about 0.25 inches $\times$ 0.5 inches $\times$ 20 mils) with about 4×10^{18} electrons per cubic centimeter having faces perpendicular to the $\langle 100 \rangle$ direction, obtained from commercial sources, was selected as a substrate member. The wafer was lapped with 305 carborundum, rinsed with deionized water, and etch-polished with a bromine-methanol solution to remove surface damage.

Four solutions were then prepared in the following manner. First, the following quantities of materials were weighed out. For solution I, 1 gm Ga, 100 mg GaAs (undoped), 2 mg Al and 15 mg Sn. For solution II, 1 gm Ga, 100 mg GaAs (undoped) and 1 mg Si. For solution III, 1 gm Ga, 50 mg GaAs (undoped), 3 mg Al and 5 mg Zn. For solution IV, 1 gm Ga, 75 mg GaAs (undoped) and 32 mg Ge. For each solution the Ga plus GaAs was briefly preheated to 900°C under H_2 in a graphite solution holder. The seed and the four prepared solutions of Ga plus GaAs were placed in separate wells in the solution holder. The remainder of the solid components which had been weighed out were then placed into the proper wells with the premixed Ga plus GaAs and were mechanically forced under the surface of the liquid Ga to insure good contact upon subsequent heating. The holder assembly was then placed into a fused silica growth tube. Hydrogen was passed through the tube to flush out air. After flushing for about 10 minutes the tube containing the holders was placed into the furnace which was at 870°C. An auxiliary heater, which consisted of a single loop of about 2 feet of 20 mil nichrome wire heated by 20 volts a.c. was disposed under the seed and was on during this operation. The temperature as measured by a thermocouple, also disposed under the seed, was allowed to rise to about 870°C and then a cooling rate of 3°C/minute was established. At 850°C the solution holder

was moved so that solution I came into contact with the seed. A mechanical vibrator was used to agitate the solution slightly while cooling to 830°C occurred. At 830°C the solution holder was moved so that solution II covered the seed and remained there with vibration for about 15 seconds. The solution holder was then again moved so that the seed was disposed under the solution III, where it was held for 30 seconds (with vibration). The solution holder was then again moved so that the seed was placed under solution IV and kept there for 60 seconds (with vibration), following which the seed holder was moved again so that a close fitting upper graphite surface of the solution holder wiped the residual of solution IV from the seed. During this entire procedure the cooling rate of 3°C/minute was maintained. Following the last step of the tube was removed from the furnace and allowed to cool to room temperature. This procedure resulted in a wafer 214 of n-type GaAs upon which were deposited, epitaxially, four layers as shown in Figs. 3 and 4. The first layer 215 on the substrate 214 is estimated to consist of n-Ga_{1-x}Al_xAs with x approximately 0.3—0.5, doped by Sn to about 10¹⁸ electrons/cm³. An n-n heterojunction 221 was formed at the interface between layers 214 and 215. The second layer 224 was GaAs doped by Si (and possibly Zn from diffusion from the following layer) compensated, but p-type. A p-n heterojunction 222 was formed at the interface between layers 215 and 224. The third layer 212 was estimated to be p-Ga_{1-x}Al_xAs with x approximately in the range 0.3—0.5 doped p-type by Zn in the range of 10¹⁸—10¹⁹ holes/cm³. A p-n heterojunction 223 was located at the interface between layers 212 and 224. The fourth layer 217 was GaAs doped p-type by Ge to about 10¹⁸ holes/cm³. This resulted on another p-p heterojunction 220 between layers 212 and 217.

The thicknesses of the layers 215, 224, 212 and 217 in a section measured were approximately 5μm, 1.5μm, 1.9μm and 2—15μm, respectively. The separation of the p-n heterojunction 222 from the p-p heterojunction 223 was therefore approximately 1.5μm.

A non-heat sunk laser diode was then prepared from the wafer so obtained for the purpose of evaluating the threshold current density. This end was achieved by initially skin diffusing Zn at high concentration (10²⁰Zn/cm³) to a depth of 0.2μm into the surface of the wafer. The substrate was then lapped to a thickness of about 6 mils. Contact (Fig. 3; layers 218 and 219) to the n and p surfaces of the wafer was made by conventional evaporation techniques whereby layers of chromium and then gold of several thousand angstroms thickness were applied. The resultant structure was then cut and

cleaved to form a number of diodes which were mounted on holders adapted with means for contacting both the n and p sides of the structures.

The resultant laser diodes were mounted in a microscope fitted for observation of infrared light and were actuated by a pulses power supply. At room temperature the threshold current density of a laser diode made from this wafer was 3900 A/cm².

Utilising similar techniques, other diodes with the intermediate region 224 less than 1.0μm thick exhibited room temperature thresholds as low as 3000 A/cm². Moreover, fully internally reflecting diodes exhibited room temperature thresholds in the range 2300—2800 A/cm².

The previously described DH laser diode also functions efficiently as an electroluminescent diode, with the omission of the optical resonator. The description which follows, however, will be limited for simplicity to an SH electroluminescent diode with the understanding that similar considerations apply to the DH. It will be appreciated that the SH electroluminescent diode does not *per se* form part of the invention.

Referring to Fig. 2 of the drawings the basic single heterostructure, as before, comprises contiguous semiconductor layers 112 and 114 of different band gaps with a p-n homojunction 125 located in the narrow band gap layer 114 and separated from a p-p heterojunction 123 located at the interface between the layers. A current source, 118, connected across contacts 120 and 122, respectively, deposited on the side of layer 112 and the bottom of layer 114, produces radiation 126 in the intermediate region which propagates out of the device through the wide band gap layer 112. In the embodiment shown, the narrower band gap layer 114 forms a substrate having a mesa-like or planar configuration to reduce current spreading effects therein. Moreover, the wider band gap layer 112 is formed in the shape of a dome or hemisphere, thereby to reduce reflection losses at the interface between layer 112 and the external atmosphere by increasing the portion of the radiation 126 which undergoes normal incidence at that interface. Both the mesa and dome structures improve the efficiency of the device. Efficiency is increased further since radiation generated in the intermediate region has an energy lower than the band gap of layer 112, thereby reducing absorption losses, i.e., in a conventional GaAs electroluminescent diode, the band gap of the p-region is nearly equal to the radiation energy and consequently causes higher loss due to optical absorption.

In a diode structure as shown in Fig. 2 (except that layer 112 is planar, not dome-like) spontaneous emission at about 8800 Å and about 1% efficiency has been observed.

The diode substrate 114 comprised n-GaAs doped with Sn or Si to a concentration of about 2×10^{18} — 4×10^{18} /cm³ and a layer of p-Ga_xAl_{1-x}As ($x \approx 0.3$ — 0.5) and was driven by about 10 ma of direct current. While the thickness of the intermediate p-GaAs region 124 (about 1 — 4μ) should not cause appreciable absorption losses, precise control thereof is not as important as in the laser diode. The diameter of the top of the mesa is typically about 500μ , whereas the bottom of the mesa is about 50 mils and is not critical. However, smaller diameters at the top increase efficiency by increasing the current density.

WHAT WE CLAIM IS:—

1. A light emitting semiconductor device comprising semiconductive regions of first and second conductivity types having wide band gaps and, interposed therebetween a first common conductivity type heterojunction and a second common conductivity type heterojunction spaced from the first heterojunction, the distance between the heterojunctions defining an intermediate region containing a p-n junction and having a narrower band gap region than the regions adjacent the other sides of the heterojunctions, the p-n junction being separated from the first heterojunction by a distance less than a diffusion length of minority carriers injected towards the first heterojunction and the p-n junction being spaced from the second heterojunction by a distance less than a diffusion length of minority carriers injected towards said second heterojunction and adapted so that the application of operating energy to the device provides a forward bias across the p-n junction to inject minority carriers across the p-n junction and produce radiative recombination of holes and electrons.

2. A device as claimed in claim 1, in which two opposite sides of the device provide reflective surfaces for the radiation produced by the device so as to form an optical cavity resonator.

3. A device as claimed in claim 1 or claim 2, in which the second conductivity type region is n-Ga_{1-x}Al_xAs wherein x is from 0.3 to 0.5, said intermediate region is p-GaAs and said first conductivity type region is p-Ga_xAl_{1-x}As wherein x is from 0.3 to 0.5.

4. A device as claimed in claim 3, in which a further layer of p-GaAs covers said first conductivity type region.

5. A device as claimed in claim 3 or claim 4, in which the thickness of the intermediate region is 1.5μ .

6. A device as claimed in any one of claims 1—4, in which the thickness of the intermediate region is from 0.125 to 1μ .

7. A device as claimed in claim 6, in which the thickness of the intermediate region is 0.8μ .

8. A device as claimed in claim 2 in which the threshold current density of the device is 3900 A/cm².

9. A device as claimed in claim 2 in which the threshold current density is from 2300 to 2800 A/cm².

10. A device as claimed in claim 1 in which the wide band gap region is dome shaped.

11. A device as claimed in claim 1 in which the narrow band gap region has a planar configuration.

12. A double light heterojunction light emitting semiconductor device substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

13. A double heterojunction semiconductor laser device substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

P. S. BROWN,
Chartered Patent Agent,
5 Mornington Road,
Woodford Green, Essex.
Agent for the Applicants.

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2. A device as claimed in claim 1, in which two opposite sides of the device provide reflective surfaces for the radiation produced by the device so as to form an optical cavity resonator.

3. A device as claimed in claim 1 or claim 2, in which the second conductivity type region is n-Ga_{1-x}Al_xAs wherein x is from 0.3 to 0.5, said intermediate region is p-GaAs and said first conductivity type region is p-Ga_xAl_{1-x}As wherein x is from 0.3 to 0.5.

4. A device as claimed in claim 3, in which a further layer of p-GaAs covers said first conductivity type region.

5. A device as claimed in claim 3 or claim 4, in which the thickness of the intermediate region is 1.5 μ .

6. A device as claimed in any one of claims 1—4, in which the thickness of the intermediate region is from 0.125 to 1 μ .

7. A device as claimed in claim 6, in which the thickness of the intermediate region is 0.8 μ .

8. A device as claimed in claim 2 in which the threshold current density of the device is 3900 A/cm².

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