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Light Emitting Diodes using Porous Silicon

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We describe the fabrication and characteristics of a pn junction type light-emitting diode (LED) using a porous silicon (PS) and microcrystalline silicon carbide (μc-SiC) heterojunction. The μc-SiC / PS pn junctions showed a clear rectification behaviour and a uniform red EL over an area of 1cm^2. From the relationship between the EL intensity and the forward current, the EL mechanism is interpreted as the recombination of electron-hole pairs doubly injected into the PS layer. No degradation was observed in the EL intensity during the measurement. These results mean that n-type μc-SiC serves well as an electron injector to PS. Furthermore, to tune the emitted wavelength, we have fabricated PS anodized with UV illumination (UV-PS) and porous SiC, and have formed junctions with ITO. We have successfully observed green EL for the ITO / UV-PS junction and blue EL for the ITO / porous SiC junction.

KEYWORDS: porous silicon, light emitting diode, electroluminescence, pn junction, microcrystalline silicon carbide, red, green, blue

§1. Introduction

Si is the dominant material for the semiconductor industry, because large wafers (almost 8 inches) are available with excellent quality and low cost and its device technology is well established. Therefore, the idea of realizing optoelectronic devices using Si has always been highly attractive due to the projected benefits in cost, reliability and functionality, although compound semiconductors such as GaAs and InP etc. are predominantly used in such a field. However, Si light-emitting devices have not been achieved yet because of the poor radiative efficiency of the indirect band structure.

In 1990, Canham reported that porous Si (PS) prepared by electrochemical anodization shows strong photoluminescence (PL) at room temperature.[1)] This indicates that PS has a potential to open up the prospects of Si optoelectronic devices, and since then, much interest has been given to PS.

The first step of Si optoelectronic devices is fabricating a light-emitting diode (LED). We have fabricated LEDs using a pn junction of microcrystalline silicon carbide (μc-SiC) and PS.[2,3)] Also, several authors have reported visible electroluminescence (EL) from Schottky-like junction type LEDs such as semitransparent Au / PS,[4,5)] and indium tin oxide (ITO) / PS junctions.[6)]. However, taking practical use into consideration, a pn junction type LED is promising, particularly in stability and brightness, because the injection efficiency in pn junctions is superior to that in Schottky junctions. In this paper, we describe the characteristics of the LED using a PS and μc-SiC pn heterojunction.

In further applications to color display technology, it is important to know about the opportunity of tuning the emitted wavelength.

To control the emitted wavelength, we have fabricated rapid thermal oxidized PS (RTO-PS),7) PS anodized with UV illumination (UV-PS)8) and porous SiC,9) and have observed blue and green PL from them. Then, to examine the possibility of green or blue LEDs, we have fabricated simple LEDs by depositing ITO on these PS layers. Although the ITO / PS interface seems to be inferior to that of μc-SiC / PS junction, especially in minority-carrier injection and stability, an ITO / PS junction is very easy to fabricate and sufficient for study into the possibility of green or blue LEDs. In this paper, we also describe the green EL from the ITO / UV-PS LED and the blue EL from the ITO / porous SiC LED.

§2. Red EL from μc-SiC / PS pn heterojunctions

In fabricating pn junctions using PS, there are important requirements for a junction material: Their preparation process must be below 400°C because of the disappearance of the PL due to the release of the SiH_2 surface species of PS at high temperature.10) Also, since the band gap of PS is considered to be larger than about 2eV, junction materials with a band gap wider than 2eV as well as a high conductivity are preferable for the effective injection of minority carriers. One of the materials which satisfy the above requirements is n- or p-type microcrystalline silicon carbide (μc-SiC) prepared by electron cyclotron resonance plasma chemical vapour deposition (ECR plasma CVD).11-13) The n- or p-type μc-SiC has a structure consisting of Si microcrystallites embedded in amorphous silicon carbide (a-SiC) and has an optical band gap from 2.1 to 2.4 eV and a dark conductivity from 10^{-3} to 1 S/cm. Its deposition temperature is less than 300 °C.

Figure 1 shows a schematic structure of μc-SiC / PS pn junctions. Al was used as an ohmic contact material. The fabrication procedure of the pn junctions was as follows; the substrates were (100) oriented, p-type crystalline (c-Si) wafers, and their resistivities were 0.2-0.4 or 3.4-4.5 Ωcm. The PS layers were formed for 3-5 min by electrochemical anodization in HF-C_2H_5OH solution ($HF:H_2O:C_2H_5OH=1:1:2$) using a constant anodic current of 20 mA/cm^2. During anodization, c-Si wafers were illuminated with a 500 W tungsten lamp, because the PS layer anodized with visible light shows stronger PL. Immediately after anodization, samples were transferred into an ECR CVD apparatus, and then n-type a-SiC (thickness, about 20 Å) and n-type μc-SiC (thickness, about 150-500 Å) were deposited onto the PS layers in sequence. a-SiC serves as a buffer layer for the hydrogen plasma damage.14) The ECR plasma CVD apparatus we used is a conventional one.13) The deposition conditions of n-type μc-SiC are as follows; the microwave power is 300 W, the deposition temperature is 300 °C, the gas pressure is about 5 mTorr, and the gas ratio is $SiH_4:CH_4:PH_3:H_2=1:2:0.01:190$. After deposition of μc-SiC, ITO (thickness, 600 Å) was evaporated as a transparent electrode. To ensure that the PS layer is responsible for a luminescent layer in the μc-SiC / PS junction, we confirmed that the μc-SiC film showed no PL at room temperature when it was excited with an Ar^+ laser (488 nm) which had larger energy than its optical band gap. This is because the hydrogen content of the μc-SiC films is less than several percent.15)

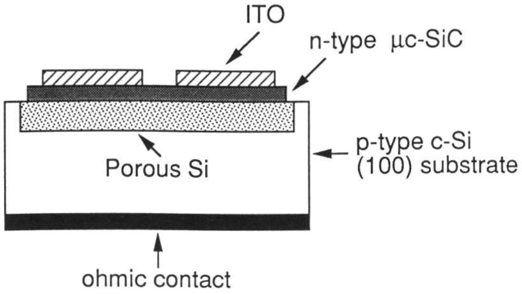

Fig.1 Schematic structure of the μc-SiC / PS pn junction.

The typical current-voltage (I-V) characteristic of the μc-SiC / PS pn junctions is shown in Fig. 2. The electrode area of ITO is 1cm^2. The forward direction corresponds to a positive potential on the p-type c-Si substrate. The rectification behaviour was clearly observed for all samples, and the rectification ratios were from 10 to 10^3 at ±5 V. Red EL was typically noticed with the naked eye at a forward voltage larger than about 15 V. However, a threshold voltage and current of the EL showed a variety of values from 15 to 30 V and from 5 to 50 mA/cm^2, respectively even for the samples which had a

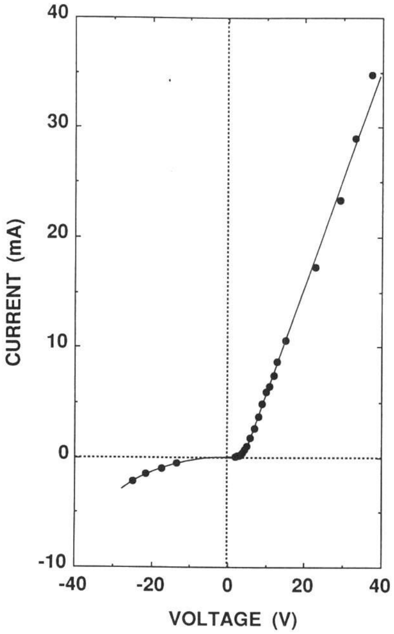

Fig.2 Typical I-V characteristic of the μc-SiC / PS pn junction.

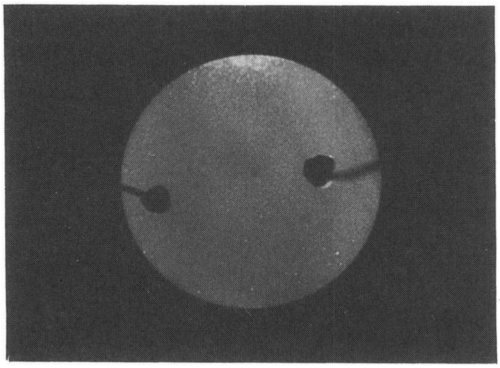

Fig.3 Photograph of red EL. The light emitting area is 1cm^2.

similar fabrication process. It is thought that this is probably due to the extent of natural oxidation of the PS surface. Figure 3 shows a photograph of the red EL. The forward current and forward voltage were 20 mA/cm^2 and 29 V, respectively. The light emitting area is 1 cm^2, which is the largest LED using PS as far as we know.

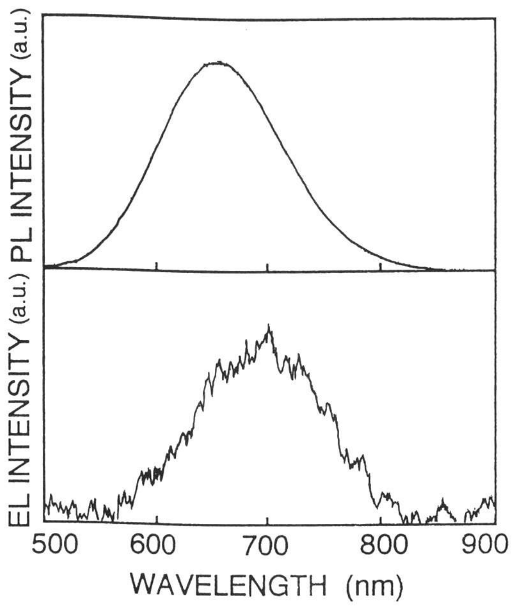

Fig.4 EL spectrum from the μc-SiC / PS pn junction. For comparison, a PL spectrum of the similar PS is also shown. The excitation light source in the PL measurement is an Ar$^+$ laser (488nm).

The EL spectrum is shown in Fig. 4, in which for comparison, a PL spectrum of the PS which was formed on a similar substrate with the same anodization condition is also shown. The forward current and forward voltage were 20 mA/cm^2 and 29 V, respectively. The EL exhibited a very broad spectrum from 580 to 820 nm with a peak of 700 nm, which is roughly similar to that of the PL. This indicates that the radiative recombination process of the EL is almost equal to that of the PL, no matter whether the recombination occurs in the crystallite interior or its surface.[16,17)]

Figure 5 shows the relationship between the EL intensity and the forward current. The EL intensity increased as the square of the forward current, suggesting that the EL is not dominated by the monomolecular recombination, but is dominated by the recombination of electron-hole pairs doubly injected into the PS layer. That is, it is found that n-type μc-SiC / PS / p-type c-Si junctions are similar to pin junctions and that electrons and holes are injected to the PS layer from n-type μc-SiC and p-type c-Si substrate, respectively. We also confirmed no light emission in the reverse direction even at the breakdown voltage of about 60 V, which also supports that the red EL is not due to an intrinsic type, but due to an injection type.

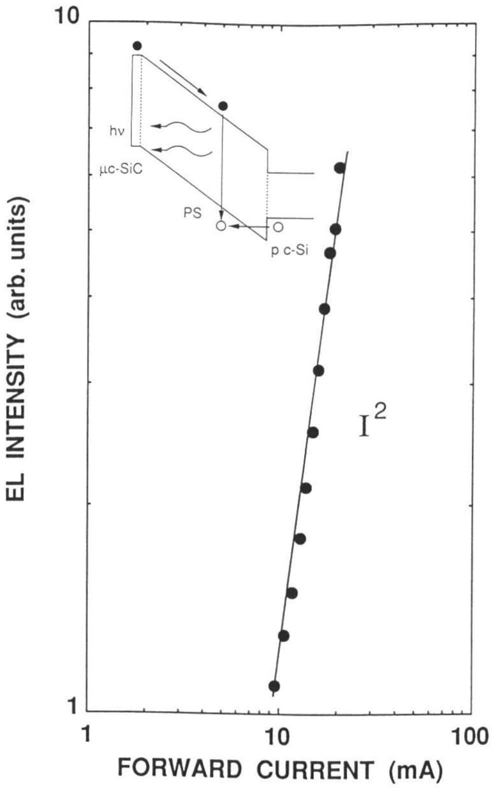

Fig.5 Relationship between the red EL intensity and the forward current of the μc-SiC / PS pn junction.

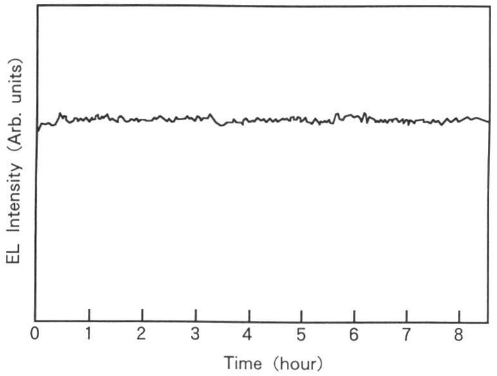

Fig.6 Red EL intensity as a function of time.

Figure 6 shows the EL intensity as a function of time. No degradation was observed during the measurement over 8 hours. These results shown in Figs. 2-6 imply that n-type μc-SiC serves very well as an electron injector to PS.

As for the quantum efficiency, it was considerably low (< 10^{-4} %). Transmission electron microscope (TEM) measurements revealed that the top surface of the PS layer only was covered with μc-SiC and a junction was not formed inside the PS layer. Therefore, the main reason for the poor quantum efficiency is probably that the light emitting area (that is, the junction region) is limited to the top surface of the PS layer. In fact, in using aqueous electrolyte as a junction material, the quantum efficiency shows a rather high value because the aqueous electrolyte soaks into the inner PS layer and sufficient contact area is the light emitting area.[18] Therefore, to improve the quantum efficiency in an LED with a solid-state electrical contact, it is important to develop how to impregnate the PS with a junction material.

§3. Green EL from ITO / UV-PS junctions

If light emission is attributed to the quantum confinement of the Si crystallites in PS, the EL wavelength depends on their size. In this case, one of the attempts to tune the EL wavelength is to prepare a PS layer with smaller Si crystallites. The method to form the PS with smaller Si crystallites is anodizing n-type c-Si under UV illumination. The basic idea is as follows: For the PS formation, holes are necessary because the inner surface of PS is covered with hydrogen and the Si surface saturated by hydrogen is inert against further attack of fluoride ions as long as no holes are available at the Si electrode. Therefore, for an n-type substrate, the light illumination is indispensable to form PS because of the generation of holes. According to the PS formation mechanism proposed by V.Lehmann et al.,[19] the band gap of the PS layer increases due to the quantum size effect, depending on the decrease of the size of Si crystallites, as the etching process proceeds. Therefore, for n-type substrates, when the band gap becomes larger than the energy of the illuminated light, the etching process automatically stops because the light can not generate holes any more. That is, the size of the Si crystallites depends on the energy of the illuminated light.

The substrates used in this experiment were (100) oriented, n-type c-Si wafers, and their resistivities were 1.25-1.75 Ωcm. Al was used as an ohmic contact material. The PS layers were formed for 5 min by electrochemical anodization

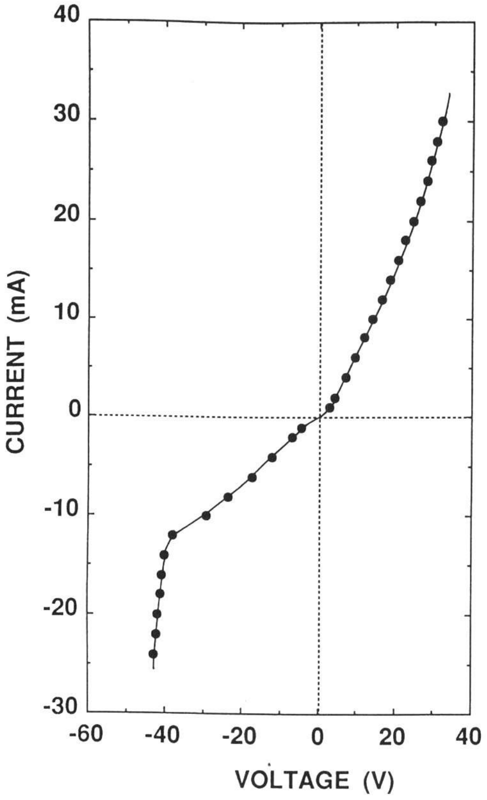

Fig.7 Typical I-V characteristic of the ITO / UV-PS junction.

in HF-C_2H_5OH solution ($HF:H_2O:C_2H_5OH = 1:1:2$) using a constant anodic current of 10 mA/cm^2. During anodization, n-type c-Si wafers were illuminated with the UV light (wavelength, from 200 to 400 nm), which was produced by filtering the light from a 150 W Hg-Xe lamp. The UV-PS shows a green PL whose spectrum is from 450 to 650 nm with a peak of 550 nm just after anodization, however it rapidly shifts to the lower energy side as far as the peak of 650 nm when the UV-PS is exposed to air.$^{8)}$ Thus, the PL spectrum of the UV-PS after fabricating the junction is from 550 to 750 nm with a peak of 650 nm. The junction was produced by depositing ITO (thickness, 600 Å) onto the UV-PS layer. The ITO area was 5 x 5 mm^2.

Figure 7 shows a typical current-voltage (I-V) characteristic of the ITO / UV-PS junctions. The samples did not show the a clear rectification behaviour. Similarly, green EL from the whole electrode area of 5 x 5 mm^2 was observed for both polarities with the naked eye. Figure 8 shows a spectrum of the green EL at a reverse voltage of 42 V and a reverse current of 20 mA. It was from 350 to 750 nm with a peak of 520 nm. The relationship between the EL intensity and the reverse current is shown in Fig. 9. The EL intensity increases linearly with the current, suggesting that the EL is dominated by the monomolecular recombination.

As mentioned above, we have succeeded in observing green EL by preparing the UV-PS. However, to understand the relationship between the EL wavelength and the size of the Si crystallites, further experiments are necessary, because the experimental results, for example poor rectification behaviour, the EL observed for both polarities and the linear dependence of the EL intensity on the current, possibly suggest that

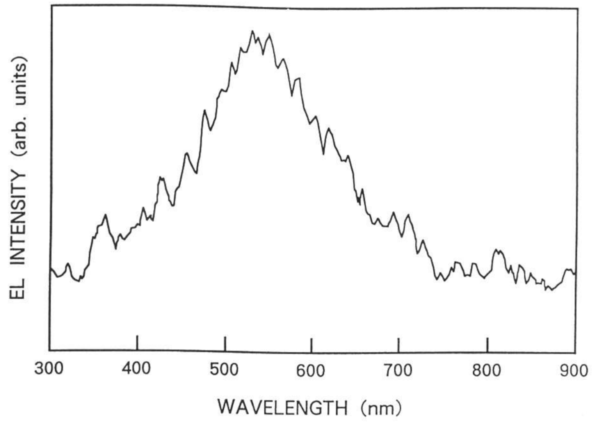

Fig.8 EL spectrum from the ITO / UV-PS junction.

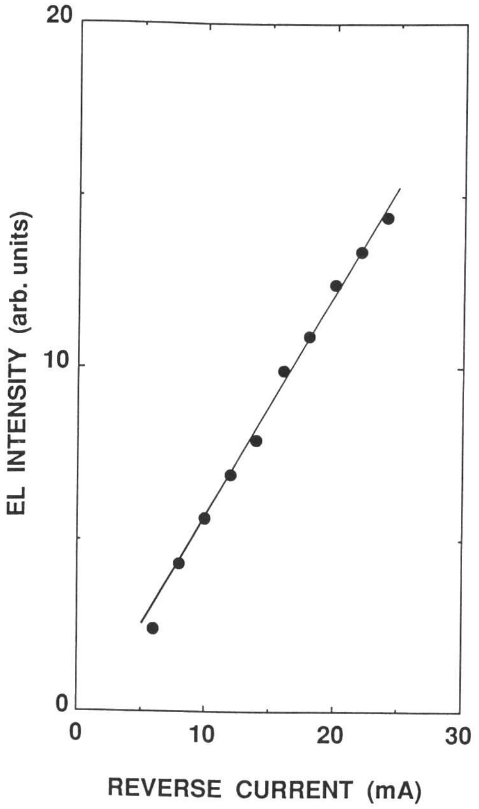

Fig.9 Relationship between the green EL intensity and the forward current of the ITO / UV-PS junction.

the mechanism of the EL is due to hot carriers. (In the case of hot carriers, we imagine that carriers may be accelerated in the a-Si:H:O layer. This is because the TEM measurements reveal that Si crystallites in the UV-PS layer are completely isolated from each other and that individual Si crystallites are covered with amorphous silicon oxyhydride (a-Si:H:O).8)) However, if it is assumed that the green PL observed just after anodization originates from the core of the Si crystallites and that the red PL after exposure to air originates from the surface of the Si crystallites,7) there is a possibility that the green EL reflects the size of the Si crystallites. In this case, blue EL might be obtained by preparing the PS with even smaller Si crystallites.

§4. Blue EL from ITO / porous SiC junctions

Using single crystalline 6H-SiC, blue LEDs have been fabricated. However, due to the indirect band gap character, the intensity of the LEDs is very low (the quantum efficiency is about 10^{-4} in Ref.20) and improvement of the intensity is strongly desired for applications such as display devices. Recently, we found that porous SiC prepared by electrochemical anodization shows much stronger blue PL than single crystalline 6H-SiC wafers.9) Therefore, we have investigated the possibility of new blue LEDs using porous SiC.

The substrates used in this experiment were (0001) oriented, n-type (0.1Ωcm, nitrogen-doped) 6H-SiC wafers grown by the Acheson method.21) Thin Ni films were evaporated on the back side of the SiC wafers to form ohmic contacts. The porous SiC layers were formed for 60 minutes by electrochemical anodization in HF-C_2H_5OH solution (HF:H_2O:C_2H_5OH =1:1:2) using a constant anodic current of 30 mA/cm^2. During anodization, n-type 6H-SiC wafers were illuminated with light from a 150 W Hg-Xe lamp without a filter. The PL intensity of the porous SiC was about one hundred times stronger than that of the n-type 6H-SiC wafers. However, the peak wavelength of the PL (about 470nm) was slightly below the band gap of the n-type 6H-SiC (430 nm) and this was different from what is expected according to the quantum confinements effect.9) After anodization, ITO (thickness, 600Å) was evaporated in an area of 5 x 5 mm^2.

Figure 10 shows a typical current-voltage (I-V) characteristic of the ITO / porous SiC junctions. The forward direction corresponds to a positive potential on an ITO layer. The rectification behaviour was clearly obtained for all samples. Blue EL from the whole electrode area of 5 x 5 mm^2 was typically observed with the naked eye from a forward bias of about 30 V. The blue EL is observed in the forward direction only. The EL spectrum is shown in Fig. 11, in which for comparison, a PL spectrum of the porous SiC which was formed on a similar substrate with the same anodization condition is also shown. The forward voltage and forward current were 40 V and 23 mA, respectively. The EL exhibited a very broad spectrum from 350 to 750 nm with a peak of 470 nm, which is roughly similar to that of the PL. This indicates that the radiative recombination process of the EL is roughly equal

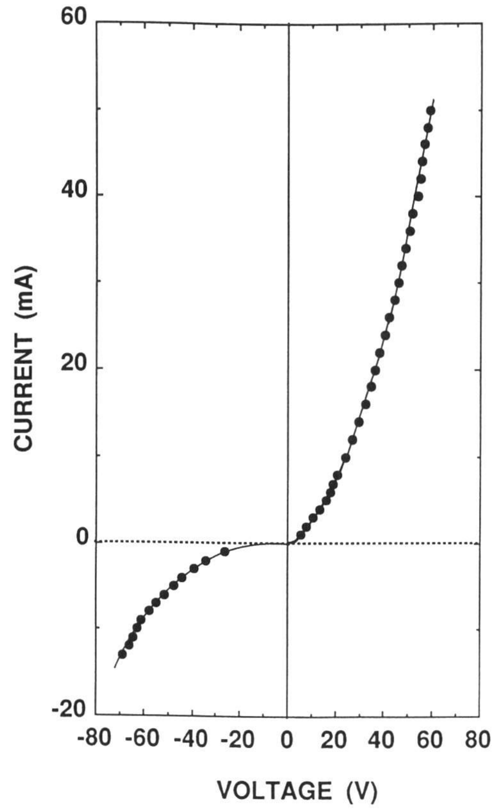

Fig.10 Typical I-V characteristic of the ITO / porous SiC junction.

to that of the PL. For the PL mechanism in porous SiC, the results in the PL spectra and picosecond PL decay measurements suggest that the origin of the strong PL is probably due to the luminescent surface states.9) That is, in the PL the carriers photo-generated in the SiC crystallites transfer from the core crystal part to the surface of the SiC crystallites and recombine radiatively at the surface. Therefore, in EL as well, the carriers are considered to recombine through the surface states of the SiC crystallites.

Figure 12 shows the relationship between the EL intensity and the forward current. The EL intensity linearly increases with the forward current, which suggests that the EL is dominated by the monomolecular recombination. However, the porous SiC / ITO junction shows a clear rectification behaviour, the EL observed in the forward direction only and the EL spectrum roughly equal to that of the PL. These results indicate that the EL is an injection type and injected minority carriers leads to the emission of a photon. Therefore, we believe that the mechanism of the blue EL is due to the recombination at the surface states of the SiC crystallites between the electrons in the porous SiC and the holes injected from the ITO electrode.

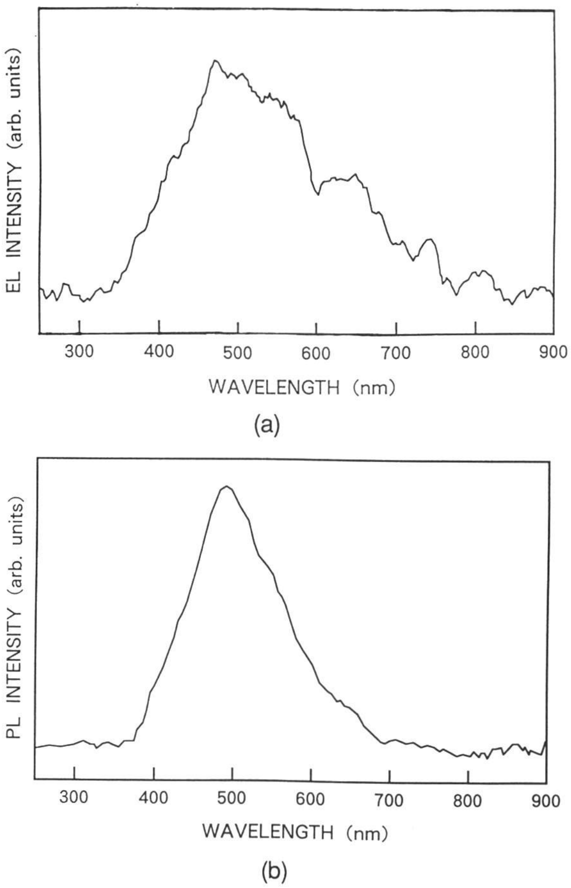

Fig.11 (a) EL spectrum from the ITO / porous SiC junction. (b) PL spectrum of the similar porous SiC. The excitation light source in the PL measurement is a He-Cd laser (325nm).

§5. Conclusions

We have described the fabrication procedure, structure, electrical properties and EL characteristics of the LED based on a pn junction of n-type μc-SiC and PS. The μc-SiC / PS junctions showed a clear rectification behaviour, and a uniform red EL over an area of 1 cm^2 at a forward voltage larger than about 15 V. The EL intensity increased as the square of the forward current, suggesting that the EL is not due to the monomolecular recombination, but to the free

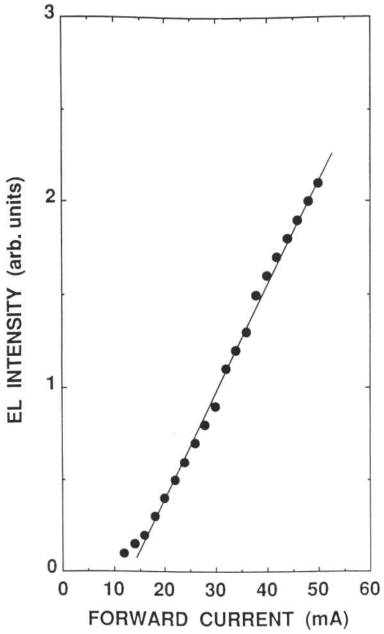

Fig.12 Relationship between the blue EL intensity and the forward current of the ITO / porous SiC junction.

carrier bimolecular recombination. The EL was stable and no degradation was recognised in the EL intensity during the measurements over 8 hours. These results mean that μc-SiC is useful as a junction material for PS. In addition to the red EL, to control the emitted wavelength, we have fabricated ITO / UV-PS junctions and ITO / porous SiC junctions. As a result, we have successfully observed green EL from the ITO / UV-PS junction and blue EL from the ITO / porous SiC junction.

Although the performance of porous Si LEDs is still too low for practical applications, continuous progress has been made especially in improving the quantum efficiency and stability and in understanding the EL mechanism. We hope that porous Si LEDs will be widely used in the optoelectronic field.

Acknowledgements

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