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Visible light emitting from the surface layer on a porous layer

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Abstract

In the present paper, the cathode luminescence (CL) spectrum of visible light emitting porous silicon (peak at 680 nm) was obtained and proved to be similar to the photoluminescence one. The CL was studied by scanning electron microscopy (SEM). The SEM photographs of the surface of the sample show that the CL only emits from the surface layer and there is no CL from the porous layer where the surface layer was moved away. The SEM photographs of the cross-section of the sample show the same result. The above experiments suggest again that the visible luminescence from the porous silicon is from the fluorescent material produced in the surface layer of the porous silicon.

1. Introduction

Recently, wide attention has been paid to the phenomenon of efficient visible luminescence from porous silicon in solid-state physics, material research and device technology because of the possibility of silicon-based optoelectronics. The current-induced light emitting device of porous silicon [1] and the highly sensitive photodetector of porous silicon [2] were fabricated in some laboratories. However, the origin of visible light emitting from porous silicon is still unknown. The main current points of view are: (1) two-dimensional quantum confinement effects in the free-standing silicon quantum wires (some consider the quantum dots now) [3]; (2) siloxene and its derivatives are produced during anodization [4]; (3) the luminescence originates from the amorphous phases [5, 6]; (4) the luminescence is related to stresses in the porous material [7].

We have reported the experiments of nonchemically obtaining the fluorescent powder from the surface of porous silicon. The photoluminescence (PL) spectrum of the powder shows the same peak position, the same FWHM and the same shape as those of the porous silicon wafer, and the powder still emits the same visible light after further grinding in an agate mortar. The X-ray photoelectron spectroscopy (XPS) and the SEM studies suggest that the visible luminescence of the porous silicon is from the powder-like fluorescent material in the surface of porous silicon [8]. We also fabricated the visible light emitting samples on the unpolished polycrystalline silicon surface using the same standard anodic oxidizing method of porous silicon fabrication. The PL spectrum of the sample was proved to be a typical spectrum of porous silicon. However, the SEM analyses of the samples show that the sample has only formed two different layers, a surface layer and a polycrystalline silicon substrate, and the visible light emitting porous silicon has three separate layers, a surface layer, a porous layer and a crystalline silicon substrate.

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The experiments suggest that the visible light of the porous silicon is not from the porous layer [9].

In this paper, we present the CL spectrum of porous silicon and the SEM photographs of the CL images of porous silicon of both the surface and the cross-section. The results of the experiments also support our point of view.

2. Experiment

2.1. Preparation of samples

Silicon wafers used in the experiments are n-type single crystals (2.4–3.6 Ω cm in the resistivity) with a mirror surface and an unpolished reverse side. In order to make the current uniform, ohmic contact on the back of the silicon wafer is achieved by evaporating a thin film of Al or introducing a solution of KCl touching the wafer's back surface when the silicon wafer's front surface is in anodic oxidation. During the anodization the sample was illuminated uniformly by a 250 W infrared lamp. The porous silicon wafers studied here are all produced by electrochemical etching in HF (48 wt%)–C_2H_5OH solution (1 : 1 by volume) at a constant current density of 80 mA/cm^2 using Pt as a counter-electrode. After the anodization, the wafers are rinsed in pure alcohol and then blow-dried in air for the test.

2.2. Spectral measurement

PL measurements: The samples are excited by the 337 nm emission of a N_2 laser with a pulse width of about 10 ns. The peak power of the laser is several hundred kilowatt (kW). By using the SPEX-1403 monochromator, the luminescence of the sample is detected by the R-928 type photomultiplier. All the data are input into a computer by a PARC-162 type boxcar integrator and the PL spectra are drawn out. All the PL experiments are carried out at room temperature.

CL measurements: The observation and the spectrum measurement of the CL from the surface of porous silicon were fulfilled in the CR-3 model cathode luminescence spectrometer. The vacuum of the sample chamber is about 10^{-5} Torr. The sample is excited by cathode rays (the cathode current is about 0.3 mA) with an energy of 11.5 KeV. The CL is detected by the photomultiplier and transferred into an electric signal. The electric signal is amplified by an amplifier and the spectrum is drawn out by a plotter.

2.3. Observation of the CL region

The CL region of porous silicon is observed using the HHS-2X model SEM. The samples are excited by an electron beam of energy 20 kev. The sample current is about 0.05 μA and the vacuum of the sample chamber is about 10^{-5} Torr. The cross-section images are visualized directly on the viewing screen.

3. Results and discussion

A typical PL spectrum of porous silicon is shown in Fig. 1. The luminescence spectrum peaks at 16 400 cm^{-1} (609 nm) with an FWHM of 3080 cm^{-1} (115 nm).

The CL spectrum of porous silicon is shown in Fig. 2. The spectrum has a peak position near 680 nm, with a FWHM of 29 nm. The CL spectrum

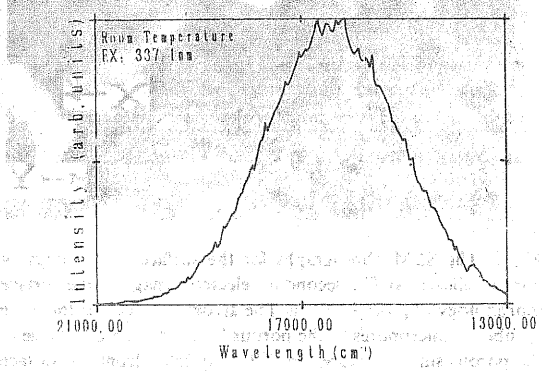

Fig. 1. A typical PL spectrum of porous silicon.

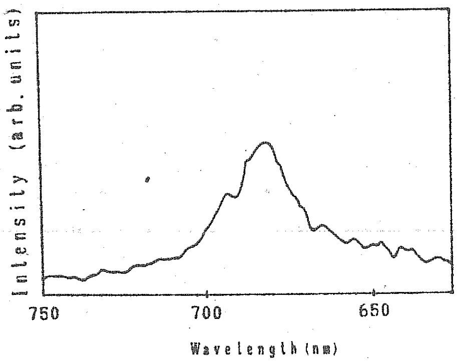

Fig. 2. The CL spectrum of porous silicon.

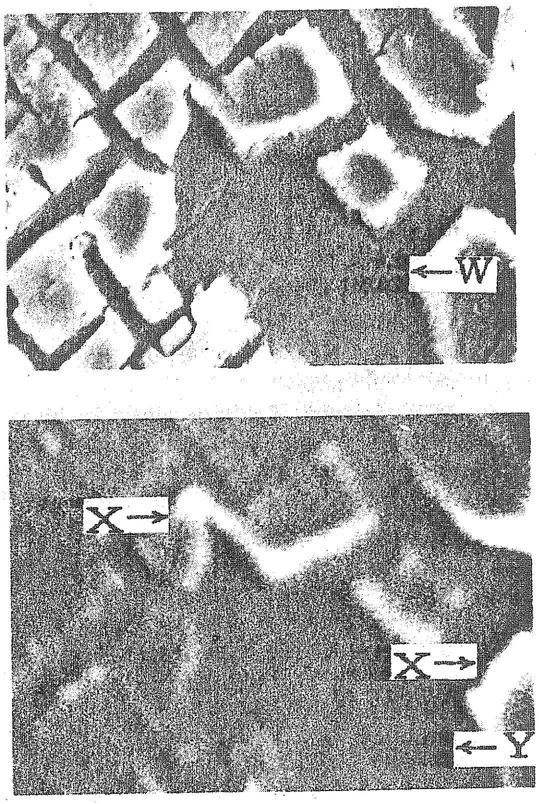

Fig. 3. The SEM photographs for the surface morphology of porous silicon. (a) The secondary electron image of the surface morphology of porous silicon. The arrow W indicates the large number of micropores of the porous layer. (b) The CL image of the porous silicon surface. The CL only emits from the surface layer (indicated by the arrow X). There is no CL from the micropores indicated by the arrow Y.

was measured from the long-wavelength direction to the short-wavelength direction. Considering that the CL intensity of the sample fades down while the sample is excited by the electron beam, the real peak position of the CL spectrum ought to be at the more short-wavelength direction and the FWHM of the spectrum ought to be more wide.

Fig. 3 presents the micrographs for the porous silicon surface analyzed with SEM. The SEM photograph shown in Fig. 3(a) is the secondary electron image of the porous silicon surface. The large number of microscopes of the porous layer is revealed at the place (indicated by the arrow W) where the surface layer has been moved off. Fig. 3(b) shows the SEM photograph of the CL image of the sample. Comparing the CL image with the porous silicon's surface morphology in Fig. 3(a), the CL only emits from the place (indicated by the arrow X) where the surface layer has not been moved off. There is no CL emitting from the micropore of the porous layer (indicated by the arrow Y) where the surface layer has been moved off.

Fig. 4 presents the SEM photographs for the cross-section of porous silicon. From right to left are the sample's crystalline silicon substrate, porous layer and surface layer. The upper section of the photograph shown in Fig. 4(a) shows the secondary electron image of the cross-section of the sample. The sample is a little tilted to the right and shows its surface on the left. The lower section in Fig. 4(a) shows the CL image of the cross-section of the sample. Comparing the upper section with the lower section of the photograph in Fig. 4(a), it is obvious that the CL only emits from the surface layer of the sample.

The upper section of the photograph shown in Fig. 4(b) is the CL image of the cross-section of the sample. The lower section of the photograph shown in Fig. 4(b) shows the CL intensity distribution which changes with the position on the cross-section (the CL intensity of the surface layer, the porous layer and the silicon crystalline substrate). The photograph proves again that the CL is from the surface layer, and neither the porous layer nor the silicon crystalline substrate emits visible light.

The spectra in Figs. 1 and 2 prove that porous silicon can also emit visible light similar to that of PL with the excitation of cathode rays. Considering

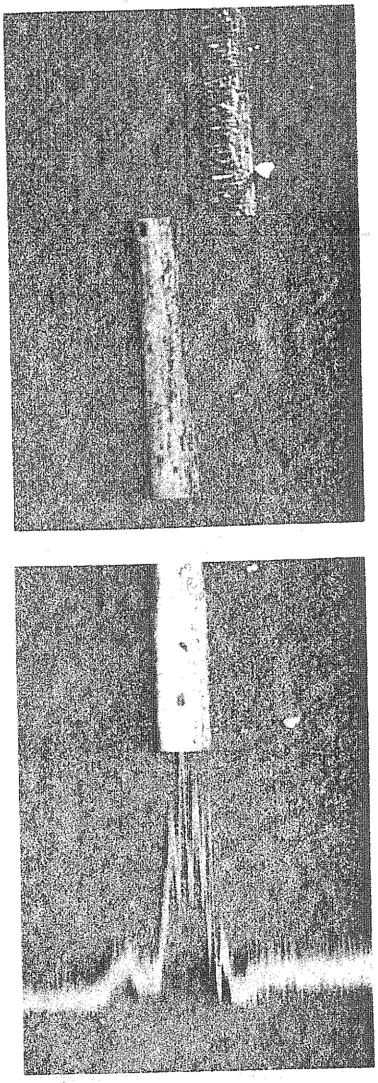

Fig. 4. The SEM photographs for the cross-section of porous silicon. From right to left are the sample's crystalline silicon substrate, porous layer and surface layer. (a) The upper section is the secondary electron image and the lower section is the CL image of the cross-section of the sample. (b) The upper section is the CL image of the cross-section of the sample and the lower section is the CL intensity changed with the position on the cross-section of the sample.

that the CL intensity will fade down with the bombardment of the electron beam, we note that the CL spectrum of porous silicon is similar to that of the PL one.

It is also observed in the SEM that the CL intensity of porous silicon will fade down with the bombarding of cathode rays. This may probably be due to the accumulated heat which does not eliminate timely. The bombardment of cathode rays does not vary the microstructure of the sample's porous layer in SEM. It is probably effective to the composition or the structure of the fluorescent material in the surface layer of porous silicon.

We have noted that the visible light emitting porous silicon can be divided into three different layers: surface layer, porous layer and crystalline silicon substrate [8]. Fig. 3 shows that the CL emits from the surface layer and there is no CL from the place where the surface layer has been moved off. The SEM photograph for the cross-section of the porous silicon in Fig. 4 shows directly that the CL is only from the surface layer, and neither the porous layer nor the crystalline substrate emits the CL. Considering all the experimental results, we suggest that the visible light from porous silicon is from the fluorescent material in the surface layer.

4. Conclusion

With the results of the spectral experiments, it is obvious that porous silicon can emit efficient visible light similar to that of PL under excitations by cathode rays. The CL will fade down during the bombardment of cathode rays.

The efficient visible light from porous silicon is from the sample's surface layer. The porous layer is of little importance to the visible luminescence from porous silicon.

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