Vol. 16 高等学校化学学报 November
1995 CHEMICAL JOURNAL OF CHINESE UNIVERSITIES 260～263

# Voltage-tunable Electroluminescence of Porous Silicon*

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**Abstract** The voltage-tunable EL was obtained upon cathodic bias of n-type PS in contact with aqueous solution containing the persulphate ion. The EL behavior as a function of the external voltage and time was investigated. The results suggest that the mechanisms of voltage-tunable EL of n-type PS cannot easily be attributed to quantum confinement effect.

**Keywords** Voltage-tunable electroluminescence, n-type PS, Quantum confinement effect

## 1 Introduction

Many studies on the optical activity of porous silicon(PS) have been carried out from the viewpoint of optoelectronic application since the discovery of its strong visible photoluminescence(PL) at room temperature [1]. However, as a useful optoelectronic material, porous silicon must provide bright electroluminescence(EL), not only PL. Several research groups have reported EL from solid state devices made from porous silicon [2,3]. Because of the high electrical resistance of the contact between conductive metal or ITO films and PS layers, the quantum efficiency of EL is very small compared with bright PL. The EL from porous silicon/solution diode was observed *in situ* during the anodic oxidation step [4]. However, such EL quenches abruptly because the oxidation reaction stops as the oxidation layer reaches a critical thickness through which few holes can penetrate. A. Bsiesy, *et al.* reported the voltage-control EL by cathodically biasing in sulphuric acid containing sodium persulphate [5]. Up to now, no other voltage-tunable EL spectra have been reported by other groups. In this paper, we present voltage-tunable EL spectra of n-type PS contact with solution. The intensity of EL as a function of the external voltage and decay time has been investigated in detail for the first time.

* Supported by the National Natural Science Foundation of China.

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## 2 Experimental

Porous silicon was formed by anodization of n-type(100) Si wafer(resistivity: 2—3 Ω·cm) in the HF-ethanol solution(HF : $H_2O$ : $C_2H_5OH$ = 1 : 5 : 5 in ratio of the weight). During the anodization process, the current density was kept to be equal to 5 mA/cm² for 10 min, and the Si wafer surface was illuminated by a 25 W halogen lamp to ensure sufficient hole ($h^+$) supply required for silicon etching. After the formation, porous silicon samples were immediately transferred into a quartz cell with a thin good optical quality window. A platinum plate served as counter electrode and Ag/AgCl electrode as reference electrode. All the potentials were referred to Ag/AgCl. The EL of porous silicon was excited in a freshly prepared 1 mol/L $H_2SO_4$ aqueous solution containing 0.2 mol/L $(NH_4)_2S_2O_8$ and a small amount of ethanol. The EL was obtained by applying constant, pulses voltage or different biases between −1.0 and −4.0 V *vs* Ag/AgCl. The emitted EL spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer.

## 3 Results

Fig. 1 shows several *in situ* EL spectra obtained at different cathodic biases. The EL signal appeared at −1.3 V(*vs* Ag/AgCl) and the peak energy shifted towards shorter wavelengths with the increasing of cathodic bias. The color of emitted light changed from orange to bright green with naked eye even in daylight. The FWHM of EL is 0.25 eV, more narrow than that of PL. Fig. 2 shows clearly the EL peak energy as a function of the applied voltage. An interesting point seen from Fig. 2 is that the peak energy is not simply proportional to the external voltage, but monotonically blue shifts with increasing of cathodic bias, then finally tends to a stable energy when the potential reaches more negative than −3.0 V. The same behavior can also be seen from Fig. 3. Fig. 3 shows the integrated intensity of the EL

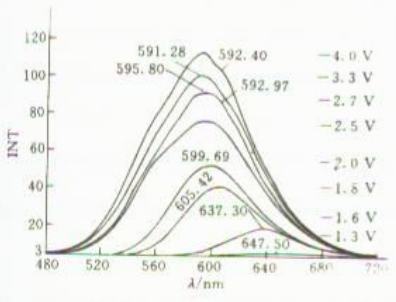



Fig. 1 EL spectra for different cathodic biases

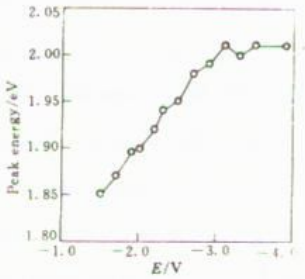



Fig. 2 Emitted photon energy as a function of the applied voltage for cathodically biased n-type PS layer

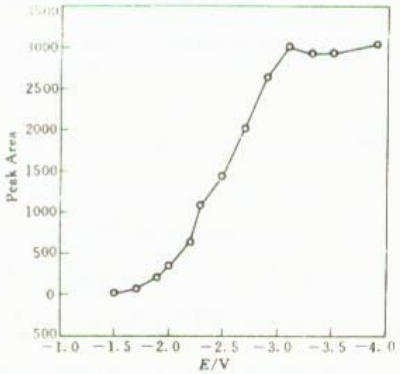



Fig. 3 EL intensity as a function of the applied voltage

signal as a function of the applied voltage. This phenomenon is different from that in Ref. 5. We wondered whether the saturation of emitted EL is the cause of electrode degeneration. In order to check the doubt, a reverse bias was applied from −4.0 to −2.0 V(*vs* Ag/AgCl). The variation of the EL with the reverse bias is shown in Fig. 4. The intensity decreased during the reverse scan. Furthermore, the EL spectra evolution was recorded as a function of time under a bias voltage of −2.5 V(*vs* Ag/AgCl) which is illustrated in Fig. 5. There were a red shift in peak energy with the prolongation of record time.

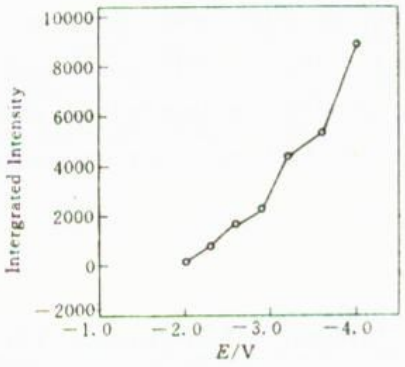



**Fig. 4 EL intensity as a function of the applied voltage(from −4.0 V to −2.0 V *vs* Ag/AgCl)**

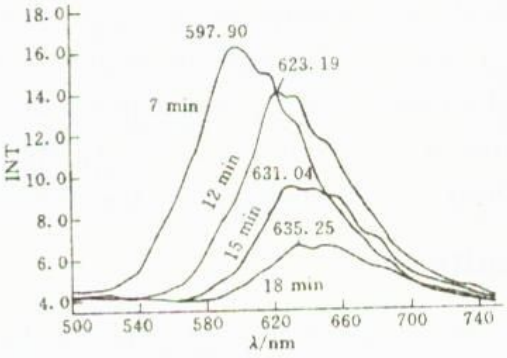



**Fig. 5 Time dependence of EL spectra of n-type PS**

## 4 Discussion

The electroluminescence of n-type porous silicon in aqueous solution containing oxidizing agent can be explained in terms of a mechanism of minority carrier injection [6]. Peroxodisulphate is well known to be reduced in two discrete steps on many semiconductors interfaces [7]. First the $S_2O_8^{2-}$ is reduced, which leads to a very reactive intermediate oxidant $SO_4^{\cdot-}$ by capture of a conduction band electron of PS.

$$S_2O_8^{2-} + e^- (CB) \longrightarrow SO_4^{2-} + SO_4^{\cdot-}$$

Second

$$SO_4^{\cdot-} \longrightarrow SO_4^{2-} + h^+ (VB)$$

The $SO_4^{\cdot-}$ has acceptor levels lower than the valence band edge of PS and therefore injects holes into the valence band of PS. Then the holes can recombine with the conduction band electrons supplied by cathodic bias to give visible light emission.

The behavior of voltage-tunable EL of PS has been explained by selective excitation of quantum-size crystallites of different dimensions in PS [5]. However, the dimensions of remnant Si walls in our EL sample were larger than 10 nm which were characterized by Raman scatter [8] and AFM [9]. It is believed that the quantum confinement effect takes place only in crystallites whose dimensions are less than 5 nm, therefore the voltage-tunable EL of n-type PS cannot easily be attributed to the quantum confinement effect. It needs further study for

fully understanding.

The saturation of the excitation of the EL shown in Fig. 2 may be related with the limit of the least size of nanometer crystallites in PS, or with some energy levels of different luminescent species on PS surface. The results in Fig. 4 and Fig. 5 confirm that the integrated intensity of EL increases with the increasing of cathodic bias. The saturation of the EL intensity shown in Fig. 3 should be due to the decay of luminescence with the prolongation of record time, not cathodic bias. The red shift of EL spectra with the extending of record time is probably due to the fact that the blue part of spectrum (high energy luminescence) is quenched first. The results suggest that different characteristic of performance may be originated form different mechanisms of carriers injection in emission of EL in PS.

In summary, the voltage-tunable EL is obtained upon cathodic bias of n-type PS in contact with aqueous solution containing the persulphate ion. The EL behavior as a function of the external voltage and time is investigated. The phenomena that the integrated intensity of EL increases with the increasing of cathodic bias and the saturation of the excitation of the EL were observed for the first time. There was not EL-max appearing in variation of cathodic biases. These results suggest that the mechanisms of voltage-tunable EL of n-type PS cannot easily be attributed to quantum confinement effect.

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(Received August 15, 1995)