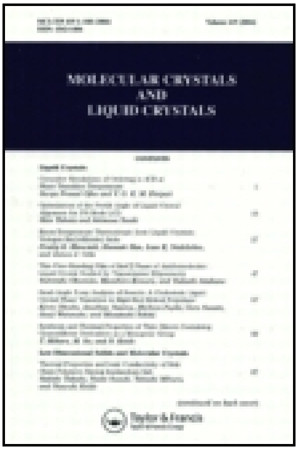

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ULTRAVIOLET ELECTRO-LUMINESCENCE IN POLYSILANE THIN FILMS

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Abstract We demonstrate for the first time that a large-area light emitting diode (LED) which generates ultraviolet (UV) light can be realized by organic-inorganic hybrid semiconductor; polysilanes (PSs). The LED based on the thin film of PS prepared by spin casting emitted 3.35 eV (370 nm) light. The emission efficiency was 0.05% at 77K and 0.01% at 190 K. Obtained results show that organic-inorganic hybrid semiconductor; PS can achieve novel properties as active material in LED device which cannot be done with pure organic or inorganic ones.

INTRODUCTION

Lately extensive studies have been made on wide-gap inorganic semiconductors such as ZnSe and GaN for the development of the light emitting diode (LED) and laser diode generating blue and ultraviolet (UV) light. Although the large area LED which emit the light in UV-region (hereafter abbreviated as UV-LED) will open various exciting applications such as full-colored display with one device and optical computers integrated with high density optical memory, these inorganic semiconductors cannot be easily used in large area devices for technological and economical reasons. In this context, organic semiconductors have great interest for application to LED[1] with large active area. In spite of their easiness in fabrication, the band gap energies of organic semiconductors are mainly dominated by π-π^* transition

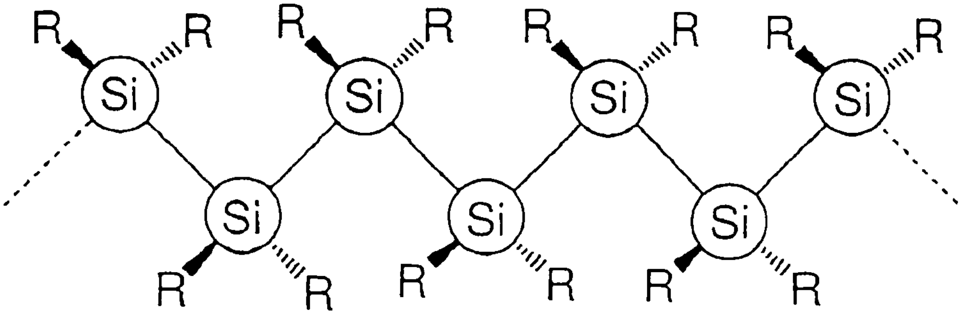

FIGURE 1 Structure of poly-(di-n-hexylsilane). R denotes the organic substituents ($R=C_6H_{13}$).

energy and limited to the relatively smaller values than those of inorganic ones dominated by σ-σ^* transition. For the progress in the large-area UV-LED, development of a hybrid semiconductor which has advantages as both organics and inorganics is important.

Polysilanes ($\left(SiRR'\right)_n$: PSs) are organic-inorganic hybrid polymers[2] and the conformation of σ-bonded backbone is maintained by organic substituents as shown in Fig.1. PSs have merits of a hybrid semiconductor as follows: The alkyl chains in substituents make PS soluble into the organic solvents and large area device can be obtained with the easy process. In addition, PS has a direct type band structure with a large gap energy (ca. 4.5eV) due to one-dimensional confinement of σ-electron on silicon backbone[3,4].

In this study, poly(di-n-hexylsilane) (PDHS: $R=R'=C_6H_{13}$) was used as a typical example among various PSs. In PDHS, absorption band with large oscillator strength, and sharp photoluminescence (PL) band with high quantum efficiency (~0.6) were observed around 3.4 eV, and 3.35 eV, respectively (see the upper part of Fig.4). These bands were attributed to the ^1B_u exciton on the silicon wire[3]. On the basis of these properties of PDHS, this polymer was expected to become an active material for LED with large active area which emits 3.4 eV light.

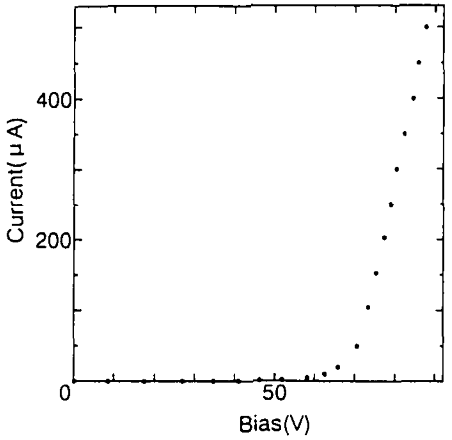

FIGURE 2 Current-voltage characteristic at 4K for a thin film device having a PDHS film of 500 nm thick and active area of 20 mm^2.

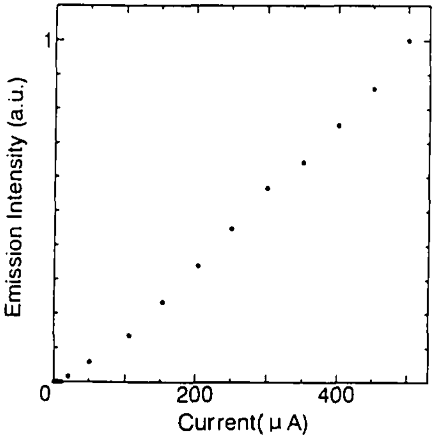

Figure 3 Integrated emission intensity plotted against current for the same thin film device giving the I-V characteristic in Fig.2.

SAMPLE PREPARATIONS

We synthesized and purified PDHS as follows: n-dichlorodihexylsilane in n-octane was added to sodium dispersion at 383K to give a 10% yield of crude PDHS as a flexible hard white elastomer. Molecular weight was ca. 300,000. The crude polymer was purified by reprecipitation from benzene-ethanol. The obtained polymer was solved into xylene, and thin film of PDHS was fabricated by spin-coating method between ITO and aluminum electrodes. The size of active area was 4x5 mm^2 with 500 nm thickness.

ELECTRONIC CHARACTERISTICS OF THE THIN FILM DEVICE

Figure 2 and 3 show electronic characteristics for the PDHS thin film devices at 4 K using ITO, and aluminum as the hole-, and electron-injecting contacts, respectively. No current and emission was observed with the inverted bias voltage lower than --70 V. In addition, integrated light output was approximately linear with current as shown in Fig.3 . Therefore we can safely conclude that the obtained thin film devices operated as a LED.

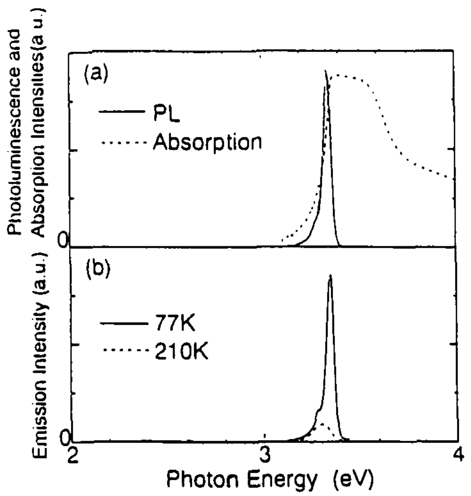

FIGURE 4 Absorption (broken-line) and photoluminescence (solid-line) spectra of PDHS thin film (a). The lower part ((b)) shows the spectrally resolved output for a LED at 77K (solid-line) and 210 K (broken-line).

We tried the magnesium and silver as a electron-injecting electrode but we could not get a good contact as aluminum. The threshold for substantial current injection was about 60 V which correspond to a field of $1.2x10^6$ V/cm (see Fig.2). The similar threshold bias field for substantial current injection was observed for the LED devices based on organic semiconductor PPV[1].

EMISSION SPECTRUM OF LED

Lower part of Fig.4 shows the spectrally resolved output for the LED at 77K and 190K observed with the direct current density of $4.5x10^{-4}$ A/cm^2. It should be noted that the spectral shape of the emission band at 3.35 eV from the LED was very sharp and well corresponded with that of PL. On the base of this data we can safely conclude that the radiative decay of ^1B_u exciton is the origin of the emission.

The quantum efficiencies (emitted photons per injected electrons) were up to 0.05% at 77 K and the emission from the LED could be seen under normal lighting although the sensitivity of human eye at 370 nm is considerably low. The emission quantum efficiencies were estimated by comparison between the light intensity generated from LED and that of the PL.

In one-dimensional semiconductors it is an important problem what the charge carriers are. In the case of LED device based on conjugated polymer such as PPV, the carriers were assigned to polarons and the origin of light emission to polaronic exciton[1,5]. In PS, the possibility of the existence of polaron and bipolaron was discussed from the theoretical point of view[6]. However, it is the reasonable consideration that the electron-lattice interaction for σ-electron is much weaker than that for π-electron and thus the polaronic effect will be considerably weak in PS[7]. In addition, there is no indication of the existence of such nonlinear excitations in the experimental data for various PSs. Therefore it is tempting idea that free electrons and holes injected from opposite sides of structure combine to form ^1B_u excitons on the silicon wire in PDHS and they decay to ground state emitting 3.35 eV light.

Previous works on PSs report that emission intensity of the thin film device in UV-region was rather weak and a broad emission band in visible region due to a deep level was relatively strong[8]. As shown in Fig.4, we have observed no such broad visible band in the PL spectra and also in the output light from the LED based on the carefully synthesized and purified PDHS.

TEMPERATURE DEPENDENCE OF THE EMISSION EFFICIENCY

The LED emission quantum yield kept constant value (ca. 0.05 %) in the temperature region below 80K and gradually decreased to nearly zero as heating up the sample until 210K as shown in Fig.5. The observed temperature dependence is quite parallel to that of PL intensity. The microscopic mechanism for the decrease in the emission efficiency of the LED and PL yield in the temperature region higher than 80 K is not clear. One possible scenario is as follows: Thermally activated structural

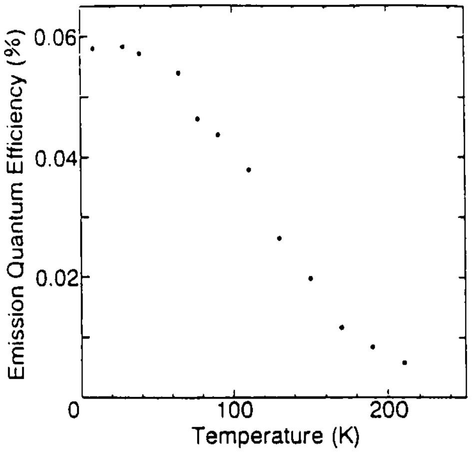

FIGURE 5 Temperature dependence of the emission quantum efficiency of the LED.

fluctuations on substituent group and backbone will decrease the delocalization of σ -electrons on silicon chain and induce the localized defect states which act as a nonradiative decay centers. In PDHS, melting of side groups and the order-disorder phase transition on backbone occur around 300 K[2,3]. This transition is gradual one and structural fluctuations may occur well below 300 K. The transition temperature of the backbone structure can be changed to much higher value and the structural fluctuation at room temperature may be considerably decreased in PS with rigid rod-like structure obtained by the design of substituents[9].

ACKNOWLEDGMENTS

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