

## Organic Ultraviolet Light Emitting Diodes

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**Abstract:** *In a short time span, highly efficient organic light emitting diodes have been developed for almost all wavelengths of visible spectrum. It is natural to extend the available emissions to ultraviolet region. Polysilanes are candidate materials for emission in ultraviolet and near-ultraviolet. The goal of our research is to develop polysilane based organic light emitting diodes for their possible application in large area electronics: a) flat panel displays, by converting ultraviolet (UV) emission from polysilanes to visible emission, b) conversion of ultra violet emission of polysilanes to white light for home lighting. This paper reports the current state-of-art in the ultraviolet emitting organic light emitting diodes and some high lights of our research in this area.*

**Keywords:** Ultraviolet light emitting diodes; Polysilanes; Degradation; Stability; Efficiency

### Introduction

For the development of UV opto-electronics, UV and near-UV emitters are required. There are very few materials that have been demonstrated to be good UV-emitters. Single crystal nitride-semiconductors, SiC, and few oxides are some of the inorganic materials that have been used to make solid-state UV-LEDs, but making single crystals, of even limited dimensions, of these materials is not easy. So, to think of large area opto-electronic devices based on these materials in near future is next to impossible. This problem could be solved if we have organic light emitting diodes with emission in UV-NUV range, but carbon based oligomers and polymers are not suitable as  $\pi$ - $\pi^*$  bandgap is not very large and there is a large Stokes' shift leading to emission in longer wavelengths [1]. On the other hand, emission from polysilanes is due to  $\sigma$ - $\sigma^*$  bandgap in UV and near-UV range and they can be easily processed as large area devices. Therefore, they are uniquely suitable for applications requiring large area and low cost UV emitters.

Polysilanes are unique material consisting of Si-backbone with organic substituent. Some non-electronic applications of the polysilanes are as silicon carbide precursors, photoresists, photo-initiators for polymerization [2]. In addition to this, they exhibit interesting opto-electronic properties such as thermochromism, doping effect, large hole mobility, photoconduction, non-linear optical properties. In contrast to  $\pi$ -conjugated polymers, polysilanes are quasi-one dimensional materials with delocalized  $\sigma$ -conjugated electrons along the polymer backbone chain. The optical and electronic properties are due to

quantum confinement effects of these  $\sigma$ -conjugated electrons. Because of their 1-D direct band gap nature, polysilanes exhibit a sharp optical absorption with a large absorption coefficient and a sharp PL with high quantum efficiency usually in near-UV or UV region [3]. Moreover, polysilane thin-films can be prepared by spin coating technique as it has good solubility in many of the organic solvents.

First reports of the electroluminescence (EL) characteristics of polysilanes, specifically polymethyl phenyl silane (PMPS), as an emissive material in light emitting diodes(LEDs) came from Fujii et al. and Suzuki in 1995-96 [4,5]. The first group is at Osaka University and Osaka R& D Laboratories, Osaka, and the second group is working at NTT Basic Research Laboratory, Kanagawa-Japan. Soon after that several papers were published reporting LEDs made of other polysilane derivatives[6-12]. In addition to the groups mentioned above the polysilane LEDs have been made by groups at Osaka Prefecture University, Tokyo Institute of Technology, and their collaborators. A problem with the polysilane LEDs initially was low efficiency and life time, and no luminescence at room temperature. NTT Basic Research Laboratory group was the first to report near-UV emission from poly[bis(p-butylphenyl) silane] (PBPS) at room temperature [13-15]. They are the only group consistently working on utilising polysilanes as an emissive material for UV or near-UV LEDs by investigating the electroluminescence (EL) characteristics in relation to the chemical, optical and electronic properties of polysilanes and the device structure [16-21].

Despite of potential emission in UV or NUV, a major difficulty is that they degrade upon exposure to UV light by scission of Si-Si bonds. In addition to degradation of polysilanes, another issue relates to absence of room temperature (RT) EL from these materials, with only exception of poly[bis(p-butylphenyl)-silane] (PBPS) [14]. Therefore, the goal of our research is to develop polysilane based light emitting diodes (LED) for their possible application in large area electronics: a) flat panel displays, by converting ultraviolet (UV) emission from polysilanes to visible emission, b) conversion of ultra violet emission of polysilanes to white light for home lighting. Specifically, our contribution to this field can be categorized in three areas:

- Understanding photodegradation in polysilanes both theoretically and experimentally. The former

involved semi-empirical, ab initio and density functional theory (DFT) calculations [22]. Experimental investigation was mainly based on optical methods [23].

- Fabrication of OLED devices using several new polysilanes. For the first time, white emission from polysilanes-OLEDs was observed along with the UV emission at room temperature. A new tunable white emitting OLED device structure is patented based on this new finding [24,25].
- Investigating the degradation behaviour of polysilane-OLED devices. A significant improvement in terms of device half lifetime has been achieved by employing the changes in the device structure and proper encapsulation.

### Photodegradation in Polysilanes

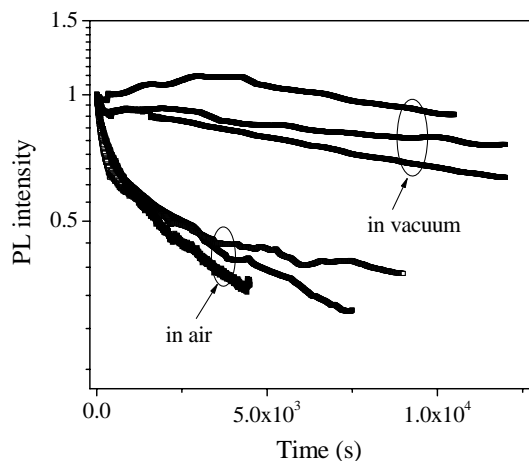
Photodegradation of diphenyl and methylphenyl polysilane copolymer in solution and film form upon exposure to ultraviolet light is investigated. Films of the polysilane were spin coated on crystalline silicon and quartz substrate by controlling the speed from 1200 to 3000 rotation per minute (RPM) and concentration of up to 20 mg/ml of the polymer in dichloromethane. Thickness measurements were done by DEKTEK profilometer. The photodegradation studies were performed on 130 nm thick polysilane films and exposed to 325 nm light from 450 W Xenon lamp. To see the effect of solvent environment from which these films can be made, the polymer degradation has been studied in vacuum and in different solvents also.

The peak PL intensity decays rapidly when exposed with 325 nm light as shown in Fig. 1 for exposure in air. Decrease in PL intensity can be interpreted as a decrease in number of segments in the polymer due to the degradation process. Therefore, PL emission at a given wavelength is proportional to number of segments that contribute to emission at that wavelength. During photodegradation, the Si-Si bonds are broken and intermediate silyl radicals are formed before any reaction takes place. As a first order approximation, we can assume that if secondary reaction occurs following Si-Si bond scission, the product of photodegradation does not participate in absorption and emission of photons. This means number of segments responsible for PL emission is decreasing due to secondary reactions with the environment, while re-link process regenerates the original segment. Since there is no change in the number of segments due to re-linking, the degradation kinetics will be decided by the rates of photoscission and secondary reaction with the environment.

### Effect of environment on photodegradation

To see the effect of environment on photodegradation of the copolymer, the peak PL intensity was also monitored in vacuum upon exposure to 325 nm light for extended period of times. The log-linear plot of PL intensities of polysilane films as a function of exposure time, in air and vacuum are compared in Fig. 1 for three different samples. The PL intensity decreases with two

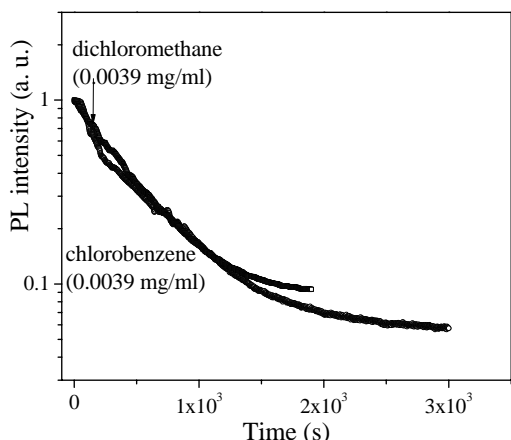
different regions in air, initially the decay rate is fast, which is then followed by a slower component. In contrast, when the films are exposed in vacuum, there is substantial reduction in the PL decay rate. The rate of reaction of free radicals is decreased in vacuum leading to change in the degradation rate. Moreover, there is also a region where enhancement of the PL emission is taking place. This enhancement in PL of polysilanes could be due to the conformational changes as a result of local heating in the sample when exposed to light [20]. The heating may result in an extended conformation of the polymer giving higher intensity in the PL.



**Figure. 1.** Log-linear plot of PL intensity at 368 nm as a function of exposure time in (a) air and (b) vacuum; the decay rate is substantially reduced in vacuum.

### Photodegradation in solution

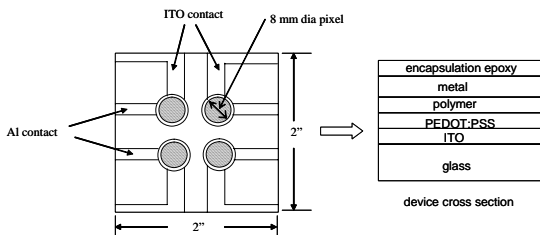
To demonstrate the effect of phase, degradation behavior of the copolymer is also studied in solution form. Dichloromethane (DCM) and chlorobenzene (CBZ) were used as solvents to see the effect of aliphatic and aromatic polar solvent. Fig. 4 shows the variation in PL intensity of polysilane copolymer in DCM (0.0039 mg/ml) and CBZ (0.0039 mg/ml) during the irradiation with 325 nm light. There is no significant difference in PL degradation for the two solvents. However, polysilane degradation rate is faster in solution. This can be explained by cage effect. The rate of re-linking of silyl radical, formed due to photo-scission will be more in films due to the larger cage effects as the molecules come closer.



**Figure. 2.** Variation in PL intensity of polysilane solution in dichloromethane (DCM) and chlorobenzene (CBZ).

**Polysilane-OLEDs**

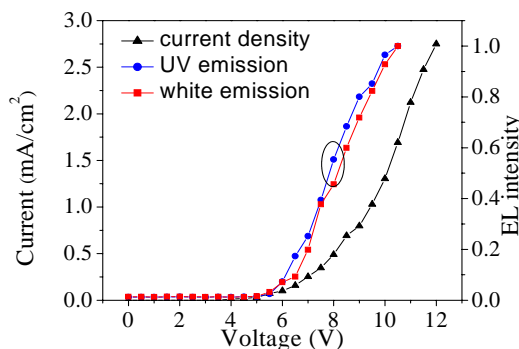
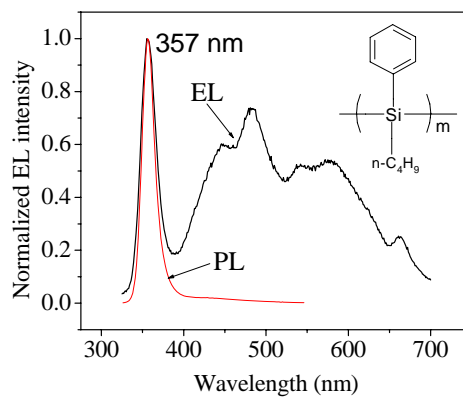
The room temperature EL emission spectra of LEDs with layer structure of ITO/ PEDOT:PSS/ polysilane/ Ca/ Al, are shown in Fig. 3. The polysilane OLEDs yielded an EL emission in deep UV in all cases. The best room temperature UV emission prior to this report was from poly[bis(p-butylphenylsilane)](PBPS) at 407nm [14]. The complete EL spectra of the devices shown in the Fig. 4 consists not only of a strong emission of UV light, but also a broad visible emission [24].



**Figure. 3.** Structures of the electroluminescence device.

As also indicated in Fig. 4, the origin of the UV emission from the device is consistent with the PL emission of respective polysilane. Thus, it arises from the bulk of the polysilane. However, the visible spectrum is only available in EL, and not seen in the PL spectrum.

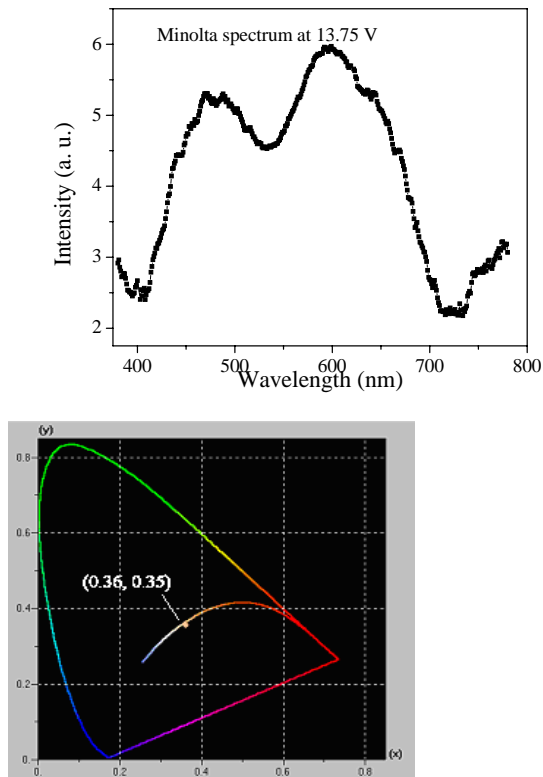
The light-voltage (L-V) characteristics of the OLEDs are shown. The L-V follows similar to the I-V curve. Both, the UV and visible emission appear together and then increase with the current.



**Figure. 4.** The EL spectra of the devices, PL and EL spectra are independently normalized to intensity of their respective UV peaks and typical Current-light-voltage (I-L-V) characteristics of the device.

**Polysilane as a white light source**

Since in these devices we have broad visible emission, radiometric Commission Internationale de l'Eclairage (CIE) coordinate of the white emission, as recorded with Minolta for PS-4 based LED is shown in Fig. 5. It can be seen that the colour of the broad emission from the PS-4 device is near to the equi-energy point (0.33, 0.33) that corresponds to pure white light. Additionally we have UV emission from these devices and hence the existing CIE coordinates can be easily tuned to desired chromaticity by exciting appropriate phosphors/dye dopants.



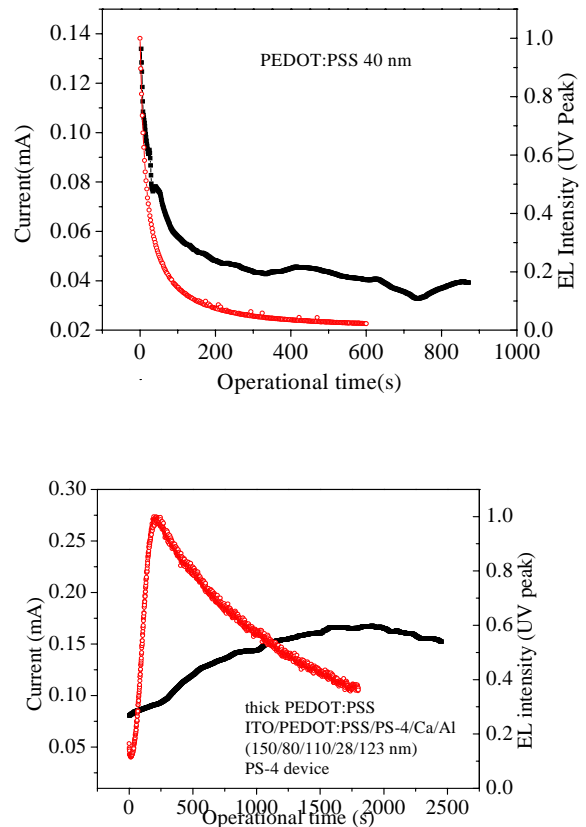
**Figure. 5. The chromaticity co-ordinates of the broad visible spectrum available from the device corresponds to a CIE coordinate of (0.36,0.35).**

**Lifetime and degradation**

Since operational stability is the major concern in OLEDs for commercial applications, we studied the degradation behaviour of these devices. The lifetime of OLEDs/PLEDs is described by the time in which the EL intensity reaches half of its initial intensity. The lifetime of initial devices was typically less than five minutes when operated under constant voltage mode.

**Effect of PEDOT:PSS thickness on device performance**

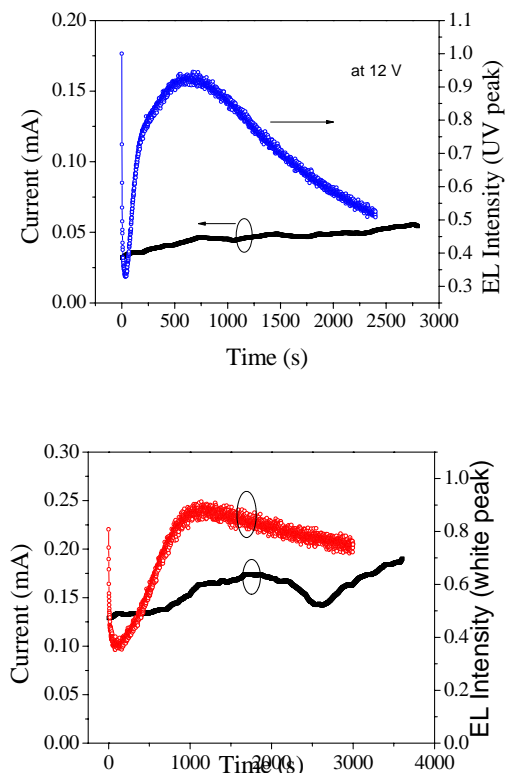
ITO surface roughness is one of the factors that contribute to the shorter lifetime in OLEDs/PLEDs. In this regard, when the PEDOT:PSS layer thickness in the polysilane device is increased from 40 nm to 80 nm, the degradation is delayed. Additionally, we observe an initial enhancement in the EL intensity as shown in Fig. 6. The durability of the device was improved in comparison to the devices made with thin PEDOT:PSS layer (40 nm). The half life of the device during continuous operation (at constant voltage) was increased from <5 min. to 19 min. with thicker PEDOT:PSS layer.



**Figure. 6. Improvement in the lifetime of polysilane device by thicker PEDOT:PSS layer.**

**Effect of encapsulation on the device performance-**

Since in unencapsulated devices, Ca cathode was getting oxidized while testing the device, therefore these devices were encapsulated using a UV cured epoxy. Fig. 7 shows the performance of the encapsulated device, where EL intensity and current is shown as a function of operational time. The operational half lifetimes of encapsulated devices were more than twice (48 min.) in comparison to unencapsulated (19 min.) devices. Half lifetime for white emission for this device is 133 min. indicating that there are two different sites responsible for white and UV emission. This shows that the encapsulation effectively protects the device from moisture and oxygen and prolongs the operational lifetime of the OLEDs/PLEDs.



**Figure 7.** EL intensity and current for UV and white emission in ITO/PEDOT:PSS/PS-4/Ca/Al (150/80/95/27/250 nm) device as a function of operational time.

In Fig. 7 it is shown that there is an initial EL enhancement for both UV and white emission. After the enhancement, the ultimate decay in the EL intensity is seen. When the bias is released for sufficient time and the device is again switched on, the EL intensity although is much lower, but again there is an enhancement until it follows the same path as it was before when the device was switched off. This phenomenon not only occurs in the declining region but also in the enhancing region (not shown here). A similar behaviour is seen for white emission also. The enhancement is due to either thermochromic effect or improvement in the contact with the cathode/anode as a result of thermal annealing effect during operation.

### Conclusions

The photodegradation of a copolymer based on diphenyl and methylphenyl polysilane has been investigated by measuring the changes occurring in PL of thin films exposed to UV light in air and vacuum. In contrast to the films, degradation in the solution is faster. The difference in the degradation behaviour of film and solution is attributed to cage effect in the film leading to re-linking of photodissociated silyl radicals.

Degradation in these materials can be reduced to some extent by avoiding oxygen and moisture.

We have also fabricated room temperature deep UV emitting polymer light emitting diodes. These devices, in addition to UV emit white light and therefore, we are proposing polysilanes as tunable white light source. Further, the device degradation issues have been explained. The device lifetime can be improved by employing thicker PEDOT:PSS layer and proper encapsulation of the device. The degradation in polysilane device is due to photo induced changes and/or creation of non-radiative defects.

The external quantum efficiency of the UV emission from these devices is estimated to be about 0.012% at 13.5 V and 0.5 mA/cm<sup>2</sup> current density (0.1 mA current). In comparison, the external quantum efficiency of the InAlGaN-based UV LEDs, a relatively matured technology, is in the range of ~0.5 -1.0 % at 20-60 mA injection. The comparison shows the possibility of developing polysilane based OLEDs as a low cost alternative to existing ultraviolet emitters.

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