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Photoluminescence properties of poly (p-phenylene vinylene) films deposited by chemical vapor deposition

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ABSTRACT

Photoluminescence spectra of PPV at varying thicknesses and temperatures have been studied. A study of the quenching of the polymer film using a modified version of fluorescence spectroscopy reveals interface effects dominating at thicknesses below about 600 Å, while bulk effects dominate at higher thicknesses. The application of the Stern–Volmer equation to solid film is discussed. Stern–Volmer plots were nonlinear with downward deviations at higher thickness of the film which was explained due to self-quenching in films and larger conformational change and increased restriction from change in electron density due to electron transition during excitation in bulk polymer films over 60 nm thick. PPV deposited into porous (~4 nm in diameter) nanostructured substrate shows a larger 0–0 than 0–1 transition peak intensity and decreased disorder in the films due to structure imposed by substrate matrix. Temperature dependent effects are measured for a film at 500 Å, right on the border between the two areas. PPV films deposited on porous methyl silsesquioxane (MSQ) were also examined in order to compare the flat film to a substrate that allows for the domination of interface effects. The enthalpies of the first two peaks are very similar, but the third peak demonstrates a lower enthalpy and a larger wavelength shift with temperature. Films deposited inside pores show a smaller amount of disorder than flat films. Calculation of the Huang–Rhys factor at varying temperatures for the flat film and film in porous MSQ shows large temperature dependence for the flat film but a smaller amount of disorder in the nanostructured film.

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1. Introduction

The photophysics of conjugated polymers have been the subject of intensive research during the last few decades mainly because of their semiconductor-like optical and electronic properties. The combination of the processability of plastics with the characteristics of semiconductors and metals has made conjugated polymers promising materials for low cost, large area optoelectronic and photonic devices. Poly (p-phenylene vinylene) (PPV) and its derivatives in particular have been useful materials in this field [1]. It is well known that the properties of the photoluminescence spectra of conjugated polymers can change depending on parameters such as ambient atmosphere [2], annealing conditions [3], and substrate temperature [4]. By manipulating these conditions, researchers have been able to tune the polymer to desirable qualities such as variable luminescence colors [5] and low turn-on voltages for polymer light emitting diodes (LEDs) [6].

Fluorescence spectroscopy (FS) is a straightforward and sensitive tool for analyzing the photoluminescence of a variety of samples. One use of FS is in the determination of the quenching capabilities of compounds exposed to certain luminescent materials, where the interaction of the quencher with the fluorophore causes a decrease in the intensity of light emission from the sample. Applications of this method use the Stern–Volmer equation to analyze materials ranging from biological sensors [7] to detection of environmental pollutants such as polycyclic aromatic hydrocarbons, where one of the advantages of this procedure is that the pollutants do not need to be separated from the bulk solution [8,9]. While the Stern–Volmer equation is most commonly used with solution based reactants and expressed in terms of concentration, it is also possible to use the method with thin films. One common application of thin film fluorescence spectroscopy is in the detection of gases such as oxygen or nitro aromatic compounds, where luminescent compounds are either embedded in a matrix or deposited as a film itself and exposed to varying partial pressures of the gases [10,11]. Other groups have modified the Stern–Volmer equation to apply to the steady-state density of hole polarons (bias voltage) or the charge injected instead of the concentration of the quencher [12,13]. Kometani et al. have

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measured the luminescence properties of multilayer assemblies of polyelectrolytes and dyes [14]. Sharma measured the quenching capabilities of I^- in a solution of a precursor polymer of PPV [15]. Encouraged by these varied results the authors have used the basic methodology applied to the system of PPV deposited onto a flat silicon substrate using chemical vapor deposition (CVD). The advantage of fluorescence spectroscopy for probing the layer structure of thin films over other probing systems such as neutron reflection [16], FTIR [17], or X-ray reflectivity [18] is the ease of use and inexpensive equipment.

The fluorescence spectra are taken as a function of the thickness of the PPV samples. The properties of the three main fluorescent transitions in the spectra can be clarified using the temperature dependent properties of the films. Temperature dependent measurements have been widely used on photoluminescent materials. Other studies commonly see results such as the intensity increase, peak sharpening, and blue shift of films with decreasing temperature [2,4,19–23]. This work applies the methodology to the thickness study mentioned above.

2. Experimental details

Poly (p-phenylene vinylene) films were deposited using the method of chemical vapor deposition in a process described in detail elsewhere [24]. Precursor material α,α' -dibromo-p-xylene was obtained from Sigma-Aldrichat 97 % purity (St. Louis, Missouri). Precursor polymer films were annealed at 250 °C under vacuum for 2 h for conversion to PPV. Film thickness varied from 100 to 2000 Å on substrates of either silicon with oxide or porous methyl silsesquioxane (MSQ). Thickness and index of refraction measurements were made on a VASE Research Spectroscopic Ellipsometer (M-44, J. A. Woollam Co., Lincoln, Nebraska) and interpreted using a biaxial Cauchy model. The depth profile of PPV in MSQ was obtained using Nuclear Resonance Analysis (NRA) of ^{12}C , since PPV is primarily carbon based. ^{12}C exhibits a strong (α,α') elastic scattering resonance in the energy region ~ 4.3 MeV. At this energy the cross section is more than 2 orders higher than the Rutherford cross-section and therefore small changes in carbon concentration can be detected. Analysis of the NRA data was done in a manner similar to Jezewski et al. [25] and Juneja et al. [26] but

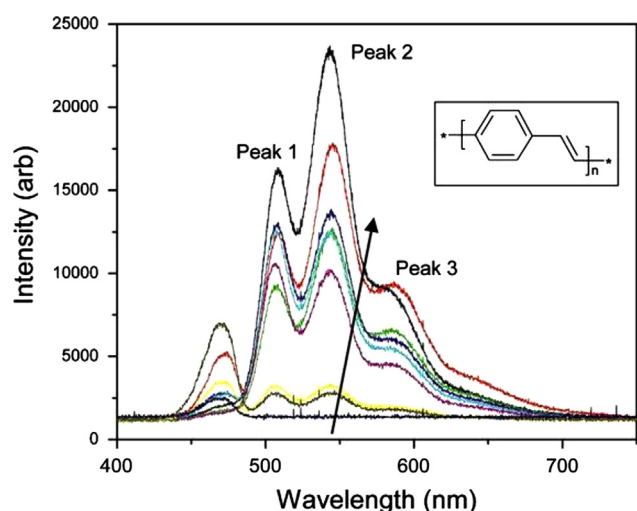


Fig. 1. Photoluminescence spectra at increasing thicknesses. In the direction of the arrow, the flat PPV thicknesses are as follows: 0 Å; 166 Å; 200 Å; 478 Å; 506 Å; 529 Å; 830 Å; 926 Å; and 2000 Å. The three labeled peaks correspond to vibronic transitions $0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ for Peaks 1, 2, and 3, respectively. The remaining peak at ~ 470 nm is due to the reflection of the excitation source light because the thickness of the film does not exceed the penetration depth. Spectra were recorded at room temperature. Inset: PPV monomer unit.

using a stoichiometric carbon content of C_8H_6 for PPV instead of C_8H_8 for parylene.

Photoluminescence (PL) spectra were measured with an Ocean Optics USB4000 Spectrometer (Dunedin, Florida). The light source was a USB-LS-450 attachment using an LED with a peak wavelength of ~ 470 nm. Low temperature measurements from 180 K to 340 K were taken in a small vacuum-pumped chamber with a SiO_2 window. After the chamber was put under vacuum with a mechanical pump, it was disconnected from the pump and vapor from liquid nitrogen was flowed in to cool the sample. Temperature measurements were made with a ceramic wire-wound platinum RTD element (Omega Engineering Inc, Stamford, CT). Heating was done with a resistive element in the sample holder. After PL measurements at low and high temperatures, samples were returned to room temperature. A repeat of the PL measurement at room temperature again verified that the spectrum matched the spectrum taken before heating or cooling and did not remain permanently changed, indicating that the changes in the spectra were due to temperature effects only and not from permanent degradation.

3. Results and discussion

3.1. Thickness dependence

Photoluminescence spectra of PPV at varying thicknesses are given in Fig. 1. As the thicknesses increase, the overall intensity increases and the relative intensities of the peaks change. All graphs have the characteristic shape of PPV photoluminescence spectra [27] and an additional reflection peak at 470 nm from the excitation source. Three peaks have been labeled: Peak 1 at 505 nm is assigned to the $0 \rightarrow 0$ vibronic transition, Peak 2 at 545 nm is the $0 \rightarrow 1$ transition, and Peak 3 at 590 nm is the $0 \rightarrow 2$ transition, as discussed further in the next section. For films around 200 Å, Peaks 1 and 2 are very small while Peak 3 is virtually indistinguishable from the background. As the thickness increases, so does the overall intensity of the spectrum as well as the separation between the peaks. Additionally, as the films increase in size, the second peak increases its intensity relative to the first peak to become the largest peak. This relative increase of the $0 \rightarrow 1$ transition has been attributed to a decreased contribution from interfacial excitons [28].

The methods of fluorescence spectroscopy may be useful when applied to the PPV/Si system. One of the most important equations in FS quenching studies is the Stern–Volmer equation (Eq. (1)) that describes the behavior of a fluorescent system while it is being quenched.

$$I_0/I = 1 + K_{sv}[Q], \quad (1)$$

In Eq. (1), I_0 and I refer to the fluorescence intensities of the compound of interest (hereafter referred to as the fluorophore, F) in the absence and presence of quencher Q, respectively, while K_{sv} is often referred to as the Stern–Volmer constant and directly relates to the binding and/or rate constants of the analyte and the quencher depending on the types of quenching involved in the samples. The Stern–Volmer equation can describe situations involving either dynamic (collisional) or static (binding) quenching. Both quenching types require contact between the F and Q molecules. In the case of dynamic quenching, contact between the excited fluorophore causes energy to transfer from F to Q, thereby preventing F from emitting radiatively. In this case the Stern–Volmer constant relates to the rate equation of the reaction. In static quenching, on the other hand, F and Q form a complex that is incapable of fluorescence in the same way that F alone was. K_{sv} is then related to the binding constant of the complex.

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