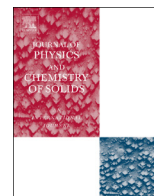




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Changes in the optical properties of as-deposited plasma polymerized 2,6-diethylaniline thin films by iodine doping



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ABSTRACT

In this study, plasma polymerized 2, 6-diethylaniline (PPDEA) thin films of different thicknesses were synthesized using a glow discharge plasma polymerization method. Scanning electron microscopy showed that the surface morphology of an as-deposited PPDEA thin film was comparatively smooth after iodine doping. The iodine-doped PPDEA was found to be thermally stable up to ca about 560 K, which was slightly lower than that observed for as-deposited PPDEA. Ultraviolet-visible spectroscopic analyses demonstrated that iodine doping resulted in a significant decrease in the optical energy gap. As the doping period increased, the direct optical transition energy gap was reduced from 3.56 to 2.79 eV and the indirect optical transition energy gap was decreased from 2.23 to 1.97 eV. Thus it is observed that, the optical parameters of as-deposited PPDEA thin films with different thicknesses can be modified with different iodine doping periods.

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1. Introduction

The plasma polymerization technique has attracted much interest in the organic electronics industry because of its capacity to synthesize thin, uniform, and homogeneous polymer films readily on a variety of substrates from almost any type of organic vapor, with thicknesses ranging from ca 10 to 1000 nm. This technique is superior to other conventional techniques that involve chemical and electrochemical polymerization because it has the advantage of solvent-free operation and it generates thin films with good chemical inertness, mechanical properties, thermal stability, weather resistance, and they are easily shaped [1–3]. Plasma polymerized thin films are produced via the recombination of reactant fragments in the form of ions and free radicals by a plasma discharge, and they can increase to a high molecular weight on a substrate in the form of branched and/or cross linked three-dimensional networks [1]. The device performance is influenced by different surface compositions, but plasma polymerized thin films have been extended to applications such as light-emitting devices, photodiodes, sensors, light guide materials, and coatings [2].

The plasma polymerization method normally yields cross-linked, branched, and generally insulating thin films, thus modifications of their physical properties by different procedures, such

as doping, heat treatment or pyrolysis, and swift heavy ion irradiation, allow their possible use in new technological applications. Bhuiyan and Bhorasker [4] synthesized and modified plasma polymerized acrylonitrile (PPAN) thin films by post-pyrolysis and iodine doping. X-ray photoelectron spectroscopy analysis showed that the iodine formed a charge transfer complex between iodine and PPAN. A significant decrease in the optical band gap (E_g) was observed due to iodine doping and pyrolysis. Saravanan et al. [5] investigated pristine and swift heavy ion irradiated PPAN thin films, where the reduction in E_g was evaluated due to the increase in the ion fluence. Kumar et al. [6] performed optical and electrical investigations of plasma polymerized pyrrole (PPPy) and determined E_g values of 1.3 and 0.8 eV for the undoped and iodine-doped PPPy films, respectively. Scanning electron microscopy (SEM) analysis showed that the surface morphology of the PPPy film was smoother with iodine. Thus, previous investigations have considered the effects of doping on organic polymers prepared using different techniques, where the results have indicated the high potential for changing the conductivity or E_g by several orders of magnitude. Various doping techniques have been performed widely using gaseous, solution, and electrochemical approaches [7]. Nitrogen (N) gas was employed as a dopant in thiophene plasma polymer thin films deposited using the radio frequency (rf) plasma-enhanced chemical vapor deposition method, where E_g broadened as the N flow rate increased because the electron densities decreased when N ions were substituted into carbon sites in the films [8]. Solid polymer electrolyte films based on poly(ethyleneoxide) (PEO) were prepared using the solution cast technique and complexed with lithium hexafluorophosphate,

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ethylene carbonate, and amorphous carbon nanotube. After the addition of various weight percentages of salt, plasticizer, and filler to the PEO matrix, E_g decreased from 5.92 to 4.60 eV for direct transitions and from 5.70 to 4.42 eV for indirect transitions [9]. The E_g of electrochemically synthesized polypyrrole-chitosan (PPy-CHI) conducting polymer composites decreased as the CHI content increased and the improved thermal stability of PPy-CHI composite films was observed based on thermogravimetric analysis (TGA) [10]. Iodine molecules are known to possess acceptor properties and many charge transfer complex formation studies have applied iodine doping (generally iodine doping using chamber and in situ methods) to a variety of polymer thin films. Due to its low molecular orbital with an ionization potential of 7.8 eV and significant electron affinity, the iodine molecules can capture weakly localized π -electrons from the polymer macromolecule and form a charge-transfer complex [11]. Polyfluorene thin films synthesized with a double discharge plasma system exhibited a decrease in E_g after iodine doping from 3.7 to 2.4 eV [12]. Anilines are used widely in the fabrication of polymer thin films [13] and heterostructures [14], and they are promising candidates for various devices such as diodes, solar cells, and other optoelectronic devices. Aniline and its derivatives have considerable donor strength but, as donor molecules, they cannot be classified as either n-donors or π -donors because the lone pair of orbital electrons on the N atom of the amine group is involved in conjugation with the π -orbital of the benzene ring. Thus, anilines have been used widely as donors with different acceptors in many charge-transfer complex formation studies [15]. In the doped state, the backbone of the polymer comprises a delocalized π system. In the undoped state, the polymer may have a conjugated backbone, which can be retained in a modified form after doping, or it may have a nonconjugated backbone, as found in polyaniline (PAn) (leuco-emeraldine base form), which becomes truly conjugated only after p doping, or a nonconjugated structure, as in the emeraldine base form of polyaniline, which becomes conjugated only after protonic acid doping, p doping, i.e., partial oxidation of the p backbone of an organic polymer [16]. Various doping approaches have been employed to modify the E_g of PAn thin films. For example, previous studies have considered modifications of the E_g and Urbach tail width of hydrochloric acid (HCl)- and camphorsulfonic acid (CSA)-doped PAn nanofibers and ion beam-induced samples have been studied. Ultraviolet-visible (UV-vis) spectroscopic absorption studies detected three direct allowed transitions at \sim 2.64, 3.61, and 4.08 eV for HCl-doped PAn nanofibers and at \sim 2.62, 3.49, and 4.02 eV for the CSA-doped PAn nanofibers [17]. PAn thin films have often been subjected to iodine doping, which has proved to be an adaptable approach for tailoring specific electrical, optical, and thermal properties [9–12]. Pristine and iodine-doped PAn was synthesized on glass substrates using the thermal evaporation method, where the decrease in E_g after iodine doping was attributed to the formation of a polaron band in the polymer [18]. PAn thin films were also prepared by oxidative polymerization of aniline in a HCl aqueous solution at room temperature using potassium dichromate as an oxidant and doping with iodine. TGA showed that ca 6 wt% of the iodine was strongly bonded to the PAn, where this did not change even at the structural decomposition temperatures of the polymer backbones. The iodine-doped PAn also exhibited decreased thermal stability [19]. Plasma polymerized aniline (PPAn) and their derivative thin films are particularly important because of their ease of synthesis, good environmental stability [3], and high capacity for doping with iodine. Mathai et al. [20] found that the E_g of PPAn was 3.04 eV and that of iodine-doped (using the chamber method) PPAn was 1.8 eV. The reduction in E_g was attributed to the incorporation of iodine into the polymer chain, which resulted in the extension of the density of states further into the visible region

of the electromagnetic spectrum compared with the undoped case. Sajeev et al. [21] investigated the production of pristine and iodine-doped PPAn thin films using alternating current (ac) and rf plasma polymerization techniques to compare their optical and electrical properties. In situ iodine doping greatly reduced the E_g of both the rf and ac PPAn thin films. The reduction in E_g was more pronounced in the rf PPAn thin films, which was attributed to the conjugation caused by the increased power during rf plasma polymerization.

It has been shown that the donor strength of aniline increases when an CH_2CH_3 (ethyl) group is introduced onto either the N atom or in the benzene ring due to the positive hyperconjugative effects of ethyl groups. The monomer, 2,6 diethylaniline (DEA) was shown to have very high donor properties and a strong charge transfer complex can be formed by the introduction of an iodine acceptor [15]. A recent study of plasma polymerized DEA (PPDEA) thin films indicated the presence of carbon (C), N, and oxygen (O) by electron dispersive X-ray analysis. Fourier transform infrared spectroscopic analysis also suggested that the aromatic ring structure and the ethyl group of the starting monomer were retained in a thin PPDEA film [22]. The E_g values of thin PPDEA films with different thicknesses were found to be about 3.60 for direct transitions ($E_{g(d)}$) and from 2.23 to 2.38 eV for indirect transitions ($E_{g(i)}$). The change in E_g with thickness was attributed to the increased structural modification of PPDEA with plasma duration [22]. The post-deposition modifications of PPDEA thin films by heat treatment included some structural rearrangements and reductions in E_g [23]. The direct current (dc) electrical properties indicated that a charge transfer complex formed between iodine and as-deposited PPDEA thin films was responsible for an increase in dc electrical conductivity and the presence of highly polarizable molecular iodine also increased the dielectric constant. [24]. Motivated by earlier studies of iodine-doped plasma polymerized thin films and the electrical properties of iodine-doped PPDEA thin films, we attempted to tailor the optical parameters of PPDEA thin films using iodine doping in the present study. We describe the changes in the optical parameters due to iodine doping and the changes with different doping periods. We also discuss the thermal stability of iodine-doped PPDEA thin films.

2. Experimental

The chemical formula of the DEA monomer is $(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_3\text{NH}_2$ and the chemical structure has been reported previously [22]. The DEA monomer, which is a derivative of aniline, was manufactured by Aldrich Chemical Company, Germany, and was procured in liquid form. The plasma polymerized thin films were deposited using a capacitively coupled glow discharge reactor. The details of the ac plasma polymerization procedure used to synthesize PPDEA thin films of different thicknesses (100, 150, and 200 nm) from the DEA monomer by varying the deposition time have been reported previously [22]. The thicknesses of PPDEA thin films were measured using the multiple beam interferometry technique. The thickness of the film “d” was determined by the relation [25]

$$d = \frac{\lambda b}{2a}$$

where a = fringe width and b = step height of the fringes. With PPDEA thin films, a Fizeau fringe pattern is obtained, as reported previously [23].

The SEM was performed using a scanning electron microscope (S-3400 N Hitachi, Japan). The PPDEA thin films were coated with a thin layer of gold by a gold sputtering coater (AGAR Auto Sputter Coater, M-108 A, UK) to avoid the charging effect during SEM. The SEM micrographs were acquired from various locations on the samples at 35000 \times magnification. The UV-vis spectroscopic

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