p-Type Semiconductors of Aromatic Diamines Doped with $SbCl_5$

Chimed Ganzorig, Kosaku Suga, and Masamichi Fujihira*
Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8501

(Received May 26, 2000; CL-000512)

Doping of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) with antimony pentachloride ($SbCl_5$) as a method to form its *p*-type organic semiconductor material is described. UV–visible absorption and X-ray photoelectron spectroscopic (XPS) data indicated formation of radial cations and dications in TPD films doped with $SbCl_5$. This doping played important roles in hole conduction and in hole injection from an indium-tin oxide (ITO) electrode to the doped TPD layer in typical electroluminescent (EL) organic thin film devices.

Solid molecular complexes obtained from reaction of aromatic amines[1] and polyvinylcarbazoles[2] with $SbCl_5$ or iodine have been investigated for the last several decades. These types of organic materials have been studied for optoelectronic devices because of their excellent semiconducting properties. The efficient hole injection into polyvinylcarbazole–$SbCl_5$ films was first observed by Partridge[3] in 1980s.

In this study, we report physicochemical properties of $SbCl_5$ doped TPD films as a *p*-type semiconductor material. Our spectroscopic studies clearly indicate presence of radical cations of TPD in the low doped films and dications in the heavily doped films. We also demonstrate enhanced hole injection by introducing the doped TPD thin layer between an ITO anode and a hole transport layer (HTL) in such a typical organic thin film EL device as ITO/TPD/tris(8-hydroxyquinoline)aluminum (Alq_3)/M.[4] Here, M is a metal cathode with a low work function.

Substrates were ITO-coated glass plates with a sheet resistance of ca. 15 Ω/square (for UV–vis and EL) and gold plates (for XPS). $SbCl_5$ doped TPD films were prepared on the substrates by spin coating of dichloromethane solutions containing 5 mM of TPD with various amount of $SbCl_5$ (0.0018, 0.018, 0.18, 0.45, 0.90, 1.35, and 1.80 in molar ratio against TPD). The spinning rate was 1000 rpm. The film thickness was found to be 10–15 nm by atomic force microscopy. The spin coating was carried out at room temperature under the ambient atmosphere and followed immediately by vacuum drying for 1 h. Although $SbCl_5$ itself fumed strongly in moist air, the prepared solutions and films were stable. For EL devices, 75 nm thick films of TPD and Alq_3 were successively vapor-deposited on the doped TPD film (10–15 nm) on ITO followed by the sequential vapor-deposition of bilayer electrode materials as previously[5] to form a top electrode with highly enhanced electron injection ability.

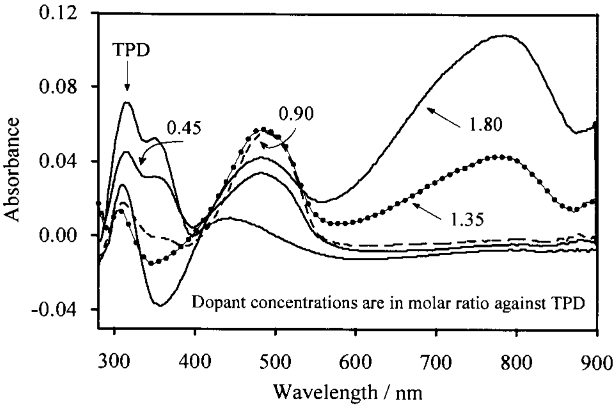

Figure 1. Effect of $SbCl_5$ concentration in TPD on the absorption spectra for doped TPD thin films spin-coated on ITO substrate.

UV–visible absorption spectra of TPD films doped with $SbCl_5$ on cleaned ITO were obtained using a Hitachi 220A spectrometer. Figure 1 shows the effect of $SbCl_5$ concentrations in the doped films on the absorption spectra. Here, the concentrations were calculated on the assumption that $SbCl_5$ was not degraded by hydrolysis during the preparation under the ambient atmosphere. As described later, an appreciable amount of $SbCl_5$ reacted with water to form HCl (confirmed with pH <1 and $AgNO_3$) in air and in solvent. With an increase in the $SbCl_5$ concentrations, the spectral changes in two-steps were clearly observed: first, the increase in absorption around 490 nm at the expense of the TPD absorption around 315 nm and then the second increase in absorption around 780 nm at the expense of the intermediate absorption around 490 nm. The first intermediate absorption band appearing around 490 nm is likely due to radical cations, while the second band around 780 nm due to dications of TPD.[6] A TPD molecule consists of two triphenylamine moieties, each of which can undergo one-electron oxidation readily, and results in finally a dication. At most, one $SbCl_5$ can receive two electrons from one TPD[7] and thus 1 mol $SbCl_5$ is enough to oxidize 1 mol TPD to TPD^{2+}. The deviation from this expected stoichiometry shown in Figure 1 can be explained by partial degradation of $SbCl_5$ by hydrolysis.

Recently, Kugler et al.[8] and Le et al.[9] studied the effect of surface treatments of ITO on N 1s core-level spectra of emeraldine base and diamine adsorbed on ITO by XPS. Figure 2 shows dependence of N 1s XPS spectra of the doped TPD films on various $SbCl_5$ concentrations. The XPS for spin-coated films on Au was performed with a Shimadzu ESCA-3400 electron spectrometer equipped with a Mg Kα X-ray source (1253.6 eV). The increase in the $SbCl_5$ concentration leads to the appearance of a new peak with a higher binding energy at ca. 401 eV.

In Table 1, we summarize the XPS data obtained for the doped films on Au. At the high $SbCl_5$ concentrations, the new peak of N 1s is clearly seen at higher binding energies by ca. 1.7–1.9 eV. This large shift can be attributed to the protonation reaction of diamine,[9] i.e. TPD, with HCl produced by hydrolysis of $SbCl_5$ during the film formation. We can also expect the change in the binding energy of N 1s by oxidation of TPD with $SbCl_5$. It can be seen from comparison between the binding energies of the N 1s peak at the lower binding energy side and the C 1s peak in Table 1 that the binding energy difference between these two peaks increases from 115.2 eV to 115.4–115.5

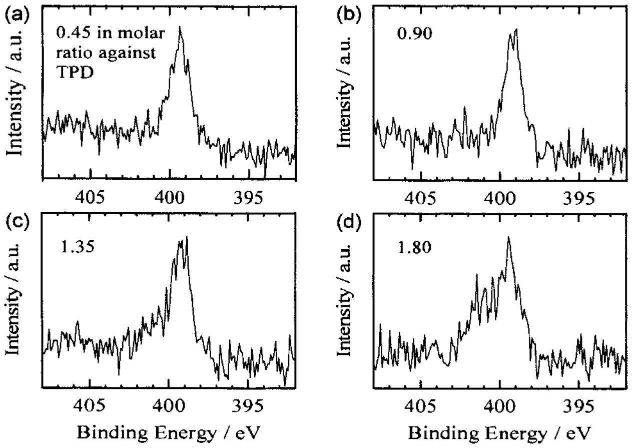

Figure 2. N 1s core-level spectra of TPD for $SbCl_5$ doped films on Au.

Table 1. XPS data for $SbCl_5$ doped TPD thin films

Dopant conc. in molar ratio against TPD	Measured binding energy, eV		
	C 1s	N 1s	Δ^a = BE(N1s) - BE(C1s)
0	284.5	399.7	115.2
0.45	283.8	399.2	115.4
0.90	283.7	399.2	115.5
1.35	283.7	399.2^b	115.5
		401.0^b	117.3
1.80	283.7	399.4^c	115.7
		401.3^c	117.6

[a] Binding energy (BE) differences between N 1s and C 1s were used to avoid surface charging effect. [b,c] Note that the N 1s binding energies were obtained from deconvolution of XPS spectra for $SbCl_5$ doped (1.35 and 1.80 in molar ratio against TPD) TPD films, respectively.

eV, and finally to 115.7 eV. The shift corresponds with the two-step change in UV–visible absorption peaks from 315 nm to 490 nm, and finally to 780 nm. In other words, the shift from 115.2 eV to 115.7 eV via 115.4–115.5 eV can be attributed to the oxidation from TPD to TPD^{2+} via $TPD^{\bullet+}$, respectively. In view of spin densities of 0.27 and 0.14 on N atoms for cation radicals of triphenylamine and *N,N,N',N'*-tetraphenyl-1,1'-biphenyl-4,4'-diamine, respectively,[10] these slight chemical shifts in XPS for the cation radical and dication formation are reasonable in comparison with the large shift due to protonation.[11]

The use of a *p*-type semiconductive thin layer between an ITO anode and a TPD layer as a HTL would enhance the hole injection efficiency of organic EL devices in the same way as *n*-type doping of Alq_3 by vapor-deposition of alkali metal[12] or by reaction of alkali metal compounds with vapor-deposited active Al atoms[5,13] at an Al cathode for enhanced electron injection. The EL characteristics were measured using an Advantest 6145 electrometer with a Topcon BM-3 luminance meter. The device structure studied was ITO/$SbCl_5$-doped(0, 0.0018, 0.018, or 0.18 in molar ratio against TPD)TPD(10–15 nm)/TPD(75 nm)/Alq_3 (75 nm)/C_6H_5COOLi(2 nm)/Al. In Figure 3, I-V and L-V characteristics of the devices with the doped TPD film for enhanced hole injection are compared with those of a device without such a layer. The device performance and the lifetime (not shown here) were improved dramatically by increasing the dopant concentration in the doped TPD film. The higher dopant concentration than 0.18 showed almost the same performance (not shown in Figure 3). We also measured characteristics of similar organic EL devices with TPD thin films doped with tris(4-bromophenyl)-aminium hexachloroantimonate, which was used recently by Yamamori et al.[14] as a dopant for a triphenylamine based polymer. The present doped TPD films with $SbCl_5$ exhibited better performance than the latter doped films.

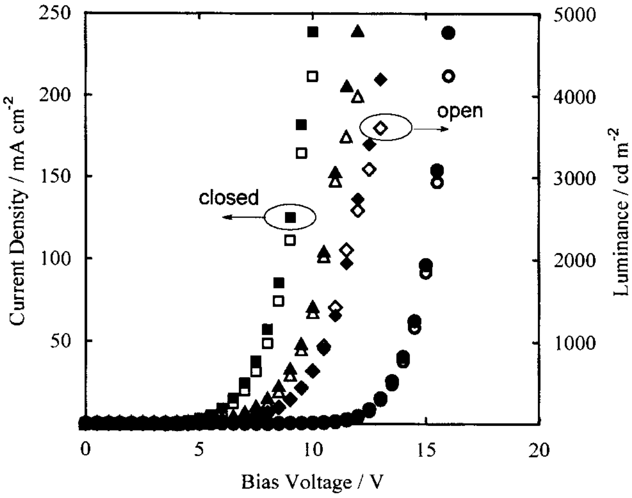

Figure 3. Current density-voltage (I-V) and luminance-voltage (L-V) characteristics of organic EL devices. Doping concentrations of $SbCl_5$ in TPD are (circles) 0, (diamonds) 0.0018, (triangles) 0.018, and (squares) 0.18 in molar ratio against TPD.

In conclusion, we have developed $SbCl_5$ doped TPD films as *p*-type semiconducting materials. The present experimental results suggest that aromatic amine films doped with $SbCl_5$ or other oxidizing reagents can be used widely as novel *p*-type organic semiconductors in the field of various electronic and optoelectronic devices.

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