Formation of Semiconducting Polymer Film by Laser CVD

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The thin films of semiconducting polymers such as poly(N-vinylcarbazole), polypyrrole, and polyaniline were formed by the laser chemical vapor deposition (CVD). The 355-nm laser excitation of N-vinylcarbazole deposited on a quartz substrate gave the poly(N-vinylcarbazole) film with the molecular weight $M_w=11860$ ($M_w/M_n=7.18$). The sandwich excimer/second excimer emission ratio of the time-resolved emission spectra suggested the isotactic structure of the poly(N-vinylcarbazole) film prepared by the laser CVD. The micropatterns of the poly(N-vinylcarbazole) with the resolution of about 20 µm were formed by the laser irradiation through a photomask. The laser flash photolysis of the N-vinylcarbazole showed the generation of the radical cation, which suggests the cationic polymerization mechanism. The optical band gap of polypyrrole film was decreased with increasing laser excitation power.

Key Words: laser CVD, semiconducting polymer, micropatterning

1. Introduction

The laser chemical vapor deposition (CVD) technique has been applied to the formation of inorganic films in microelectronics.[1] The laser CVD using the photochemical reaction of a reactant has some advantages compared to usual CVD using the thermal decomposition of a reactant on a substrate at a high temperature. The first, the laser CVD lowers the reaction temperature and reduces the damage of the substrate and the film. The second is the selectivity of the photochemical reaction induced by the wavelength-selective excitation using the laser beam. It is in contrast to the CVD using the thermal decomposition which causes side reactions and the damage of the CVD film. The third, the laser CVD is spatial selective reaction due to the coherent laser beam. The direct patterning of inorganic films by laser projection CVD has been reported.[2] Although the projection CVD enables the selective film deposition on the irradiated parts of the surface, the deposition rate of the conventional laser CVD is relatively low because of the small absorption cross section of the gas molecule adsorbed on a substrate.[3] The low-temperature condensation method has been employed to increase the deposition rate, where the laser beam is irradiated to the deposited reactants on a cooled substrate.[4] Recently, this method has been applied to the formation of insulating polymer films.[5] In the fabrication of sensors and micromachines, the combination of various kinds of films such as conducting, semiconducting, insulating, and sacrificial films is necessary. However, there is little study on the patterned deposition of conducting and semiconducting polymer films by the laser projection CVD.[6,7] In this work, we investigated the formation of poly(N-vinylcarbazole) (PVCz), polypyrrole, polyaniline films and the micropatterning by the laser CVD.

2. Method

2.1. Formation of Polymer Films by Laser CVD

The chemical structures of monomers used for the formation of semiconducting polymer films are illustrated in Fig.1. Under reduced pressure, the monomers are deposited on a cooled substrate using laser CVD apparatuses illustrated in Fig.2. The apparatus A was used for the laser CVD of a solid monomer such as a N-vinylcarbazole, where a quartz substrate was cooled to 4°C by a Peltier device (Melcor, CP 1.4-14-06L ring module) under vacuum ($10^{-5}$ Pa).
Torr) with heating the monomer at 50°C. The 355-nm laser beam (Nd:YAG laser, Quanta-Ray GCR-130, 10 Hz, 6 ns fwhm) was irradiated to the deposited monomer through the hole of the Peltier device. The laser CVD of liquid monomers such as thiophene, pyrrole, and aniline was carried out using the apparatus B in Fig.2. Under vacuum (5 x 10^{-3} Torr), a liquid monomer was condensed on the substrate cooled at -5°C by a coolant with heating the monomer at 60°C. The laser CVD was carried out by the 266-nm laser pulse irradiation to the condensed layer through a quartz window.

2.2 Characterization of Laser CVD Film.

The molecular weight Mw and the molecular weight distribution Mw/Mn of PVCz were determined by a gel permeation chromatography (GPC) using monodispersed polystyrenes as standards. The electronic absorption spectra were measured by an absorption spectrophotometer (Hitachi, U-3500). The FT-IR spectra were measured by a Fourier transform infrared spectrometer (JEOL, JIR-100). The elemental composition of the CVD films was analyzed by XPS spectra (Shimadzu, ESCA-750).

The time-resolved emission spectra were measured using an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA) pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S) with a pulse selector (Spectra-Physics, Model 3980), a harmonic generator (GWU-23PS), and a streak scope (HAMAMATSU, C4334-01, sweep repetition rate 2 MHz). In the measurements, by setting a threshold level for A/D converted CCD camera signal, the photoelectron image can be clearly separated from the noise. The system enables photon counting measurements at simultaneous multiple wavelength. Typical instrument response functions for this apparatus is 20 ps (fwhm) and the time resolution of the detection within 5 ps can be obtained by using the deconvolution technique.

The transient intermediates during the photochemical reaction were investigated by the laser flash photolysis. The excitation of a monomer was performed by 355-nm laser pulse from a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm). The time profile of the transmittance detected by a photomultiplier was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz) and analyzed by a personal computer. As probe beams, a 150 W continuous-wave xenon lamp (HAMAMATSU, L2195) and a xenon flash lamp (EG&G, FX-249u) were used for the measurements by the transmittance spectroscopy and the diffuse reflectance spectroscopy, respectively.

3. Results and Discussion

3.1 Laser CVD of PVCz

3.1.1 Formation and Micropatterning of PVCz Film

A transparent PVCz film was prepared on a quartz plate by laser CVD with the laser power of 10 mJ/cm² at 355 nm for 10 min. The chemical structure of the PVCz was investigated by FT-IR spectra. The FT-IR spectra of N-
Vinylcarbazole and PVCz by the laser CVD are compared in Fig. 3. The signals assigned to C= C stretching vibration (1639 cm\(^{-1}\)) and -C=CH\(_2\) (858 cm\(^{-1}\)) and -CH=C- (962 cm\(^{-1}\)) bending vibration of the vinyl group are disappeared in the spectrum of PVCz by the laser CVD, which suggests the polymerization due to the reaction of the vinyl group. The polymer film was dissolved to tetrahydrofuran and the molecular weight Mw and the molecular weight distribution Mw/Mn were determined to be 11860 and 7.18, respectively, by GPC. The laser beam irradiation through a photomask gave the direct patterned deposition on a substrate. The photomicrograph of the photomask and the micropatterning of the PVCz film are shown in Fig. 4. The micropatterning of semiconducting PVCz film with the resolution of about 20 µm can be obtained by the laser projection CVD method.

3.1.2 Time-Resolved Emission Spectra of PVCz Film

The emission spectra of PVCz seriously depend on the tacticity.\[8\] The emission from two kinds of excimers has been reported for PVCz.\[9\] One is the second excimer which has the partial overlap between excited and non-excited carbazole rings and shows the emission maximum at 370 nm. The other is the sandwich excimer which has the full overlap between excited and non-excited carbazole rings and shows the emission maximum at 420 nm. The configuration of two kinds of excimers are illustrated in Fig. 5. The isotactic PVCz satisfies the conformation of sandwich excimer as shown in Fig. 6. On the other hand, the syndio-
tactic PVCz needs the conformational change to form the excimer. Considering the motion of the large PVCz chain, some parts in the polymer chain inhibit the full overlap between two carbazole rings. After the laser pulse excitation, the singlet excited state migrates to a preformed excimer site by the Förster-type energy transfer between carbazole rings along the polymer chain. The ratio of the sandwich excimer formation site to the second excimer formation site for the isotactic PVCz is higher than that of the syndiotactic PVCz. The energy migration process can be observed by the time-resolved emission spectroscopy monitoring the sandwich excimer/second excimer intensity ratio.[10] In this study, the time-resolved emission spectra of PVCz prepared by the laser CVD was compared to those of isotactic and syndiotactic polymers. The radical polymerization of N-vinylcarbazole was carried out using azobisisobutyronitril as an initiator in a dehydrated and degassed benzene at 70°C for 7 hr. The molecular weight $M_w$ and molecular weight distribution $M_w/M_n$ were determined to be 162800 and 3.62, respectively, by GPC. The ratio of the isotactic sequence to the syndiotactic sequence was determined to be 1/3 by the $^1$H-NMR spectrum. The cationic polymerization of N-vinylcarbazole gives a highly syndiotactic PVCz.[11] The cationic polymerization was carried out using $\text{BF}_3\text{O(C}_2\text{H}_5)_2$ as an initiator in a deaerated toluene at 20°C for 18.5 hr. The molecular weight $M_w$ and molecular weight distribution $M_w/M_n$ were determined to be 1180600 and 16.73, respectively, by GPC. The ratio of the isotactic sequence to the
syndiotactic sequence was determined to be 1/1 by the $^1$H-NMR spectrum. Fig. 7 shows the time-resolved emission spectra of PVCz films prepared by the radical and cationic polymerization. In the first stage within 200 ps after the excitation, the emission spectra are characterized by the 370-nm band assigned to the second excimer. The excited state is trapped at the second excimer formation site just after the laser pulse excitation. With decreasing the emission intensity of the 370-nm band ($I_{370}$), the emission intensity of the 420-nm band ($I_{420}$) assigned to the sandwich excimer increases. This can be attributed to the energy migration from the second excimer site to the sandwich excimer site. The $I_{420}/I_{370}$ ratios at 1.5 ns of radically and cationically polymerized PVCz films are 0.94 and 1.18, respectively. This result can be explained by considering the higher isotactic polymer chain of cationically polymerized PVCz. The time-resolved emission spectra of the PVCz films prepared by the laser CVD are shown in Fig. 8. The emission band at 370 nm is observed within 200 ps after the laser pulse excitation, similar to the radically and cationically polymerized PVCz films. The $I_{420}/I_{370}$ ratio at 1.5 ns of the PVCz films by the laser CVD is 2.3, which suggests a highly isotactic polymer chain. The tacticity is due to the solid state photopolymerization of N-vinylcarbazole.

### 3.1.3 Intermediate During the Photochemical Reaction of N-Vinylcarbazole

The photopolymerization mechanism of N-vinylcarbazole was investigated by the laser flash photolysis. Fig. 9 shows the transient absorption spectra obtained by 355-nm laser pulse excitation of 0.5 mM N-vinylcarbazole in benzonitrile. (a) in deaerated solution, (b) in aerated solution.

![Fig. 9](image)

Fig. 9 The transient absorption spectra at 2.5 µs obtained by 355-nm laser pulse excitation of 0.5 mM N-vinylcarbazole in benzonitrile. (a) in deaerated solution, (b) in aerated solution.

The photopolymerization mechanism of N-vinylcarbazole was investigated by the laser flash photolysis. Fig. 9 shows the transient absorption spectra obtained by 355-nm laser pulse excitation of 0.5 mM N-vinylcarbazole in benzonitrile. The transient absorption spectrum of N-vinylcarbazole shows two absorption bands at 420 and 780 nm in deaerated benzonitrile. The 780-nm band can be assigned to the radical cation formed by the photo-ionization of carbazole ring. [12] With introducing oxygen, the absorption band at 420 nm considerably decreased. The quenching by the oxygen suggests the assignment of the 420 nm band to the excited triplet state. Fig. 10 shows the transient diffuse reflectance spectrum at 5 µs obtained by 355-nm laser pulse excitation of N-vinylcarbazole adsorbed on silica gel powders (5 wt%) in vacuo.

![Fig. 10](image)

Fig. 10 The transient diffuse reflectance spectrum at 5 µs obtained by 355-nm laser pulse excitation of N-vinylcarbazole adsorbed on silica gel powders (5 wt%) in vacuo.

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shows the transient diffuse reflectance spectrum at 5 μs obtained by 355-nm laser pulse excitation of N-vinylcarbazole adsorbed on silica gel powders (5 wt%) in vacuo. Even in a solid state, the absorption band at 780 nm of the N-vinylcarbazole radical cation is seen. This result suggests the polymerization mechanism via radical cation.

3.2 Laser CVD of Polythiophene, Polypyrrole, and Polyaniline

In the case of the N-vinylcarbazole, the polymerization proceeds by the photochemical reaction of the vinyl group. The monomers, thiophene, pyrrole, and aniline, have no vinyl group and the polymerization occurs by the oxidative reaction. Polythiophene, polypyrrole, and polyaniline are known as highly conducting polymers by doping, which forms a radical cation site in the π-conjugated polymer chain. The conduction mechanism has been explained by the polaron and bipolaron mechanism.[13-15] Because these polymers are insoluble to common organic solvents, the selective patterned deposition by the laser CVD is effective technique.

The polythiophene film was obtained by 266-nm laser pulse excitation of 2,5-dibromothiophene condensed on a substrate cooled to -5°C with heating the monomer at 50°C under 5 x 10⁻³ Torr. An insoluble dark brown film was obtained by the laser CVD for 5 min. The same laser CVD condition of thiophene did not give a film. This result suggests the photochemical reaction via the cleavage of the C-Br bond of the 2,5-dibromothiophene. Fig. 11 shows the absorption spectra of polythiophene films obtained by the laser CVD under various laser powers. With increasing the laser power, the absorption tail shifts to the lower energy region. The optical band gap determined by the Mott plots of the absorption spectra are summarized in Table 1. The chemical structure of polythiophene films prepared under various laser powers were investigated by FT-IR and XPS spectra. The FT-IR spectra of polythiophene by the laser CVD showed the bending vibration of the β-proton of the thiophene ring at 800 cm⁻¹, which suggests the bonding of thiophene rings at 2,5 position. With increasing the laser power, the signal of the β-proton at 800 cm⁻¹ decreased. The decrease of the β-proton suggests the increase of the disordered structure of the polythiophene film. Table 2 shows the elemental composition of polythiophene films by the XPS analysis. The polythiophene films prepared by the photochemical reaction of 2,5-dibromothiophene do not contain Br atom. This results agree with the results from FT-IR spectra which suggests the bonding of thiophene rings at 2,5 position. In Table 2, the carbon content of the polythiophene film increases from 73.5% to 77.1% with increasing the laser power from 10 to 15 mJ/cm². This suggests the carbonization of polythiophene film by the high power laser irradiation.

The conductivities of the polythiophene

![Fig. 11 The absorption spectra of polythiophene films obtained by the laser CVD with various laser powers.](image-url)
films were measured with and without the iodine-doping. The conductivities are summarized in Table 3. The conductivity of the polythio-phene film prepared at 10 mJ/cm$^2$, which has the regular 2,5-position bonding of thiophene rings, shows the increase of the conductivity about five orders of magnitude with the iodine-doping. On the other hand, the conductivities of polythiophene films prepared under the higher laser powers decrease with the iodine-doping. This may be due to the decomposition of the polythiophene at the disordered structure with the iodine-doping. The conductivities did not recovered by removing the iodine, which suggests the chemical reaction of polythiophene films with the iodine. The laser CVD of poly-thiophene with a photomask gave the micro-patterning of the conducting film with the resolution of about 50 µm.

The laser CVD of polypyrrole and polyaniline were carried out by the 266-nm laser pulse excitation of pyrrole and aniline, respectively, in the presence of carbon tetrachloride as an oxidizing agent. The photopolymerization of thiophene using carbon tetrachloride as an oxidizing agent has been reported. The electron transfer between the excited state of the monomer and carbon tetrachloride produces the radical cation of the monomer and the oxidative photopolymerization occurs. The similar photopolymerization mechanism can be applied to the laser CVD of polypyrrole and polyaniline. The pyrrole film was obtained by 266-nm laser pulse excitation of pyrrole condensed on a cooled substrate. The conductivity of the pyrrole film prepared at 10 mJ/cm$^2$ shows the increase of the conductivity about five orders of magnitude with the iodine-doping. The conductivity of the polypyrrole film with the iodine-doping was 8.7 x 10$^{-6}$ S/cm. The rather low conductivity is due to the thermal decomposition of the black polypyrrole film by the laser irradiation. The polyaniline film was also obtained by 266-nm laser pulse excitation of aniline condensed on a substrate cooled to -5°C with heating the monomer at 50°C under 5 x 10$^{-3}$ Torr. The laser CVD for 10 min gave a pale yellow film on a quartz substrate. The optical band gap was 2.46 eV. With the iodine-doping for 20 min, the optical band gap decreased to 1.65 eV and the conductivity increased to 1.5 x 10$^{-3}$ S/cm.

4. Conclusion

The micropatterning of semiconducting PVCz film with the resolution of about 20 µm can be obtained by the laser projection CVD method. The emission intensity ratio of the sandwich excimer (420 nm) to the second excimer (370 nm) of the PVCz films prepared by the laser CVD suggests a highly isotactic polymer chain due to the solid state photopolymerization of N-vinylcarbazole. The formation of the radical cation of N-vinylcarbazole was observed by the laser flash photolysis, which suggests the photopolymerization mechanism of N-vinylcarbazole via the radical cation during the laser CVD. The polypyrrole film was obtained by the 266-nm laser pulse excitation of 2,5-dibromothiophene condensed on a cooled substrate. The conductivity of the polypyrrole film prepared at 10 mJ/cm$^2$ shows the increase of the conductivity about five orders of magnitude with the iodine-doping. The polypyrrole and polyaniline films were prepared by the 266-nm laser pulse excitation of pyrrole and aniline on a cooled substrate, respectively, in the presence of carbon tetrachloride as an oxidizing agent.

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References