Thin Films

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High-Performance Two-Dimensional Polydiacetylene with a Hybrid Inorganic–Organic Structure**

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Many materials used in organic electronics are conjugated organic polymers with a backbone of alternating double and single bonds along which electrons can flow. Owing to their structural flexibility and tunable electronic properties, conducting polymers show great promise in flexible, inexpensive, large-area applications such as flexible displays, radio frequency identification devices (RFIDs), smart cards, non-volatile memory, and sensors.[1–5] The one-dimensional nature of these polymers can be misleading. Thin films of conjugated polymers still have disordered structures, with twists and bends in their individual polymer strands. For most applications, the challenge is to uniformly align the polymer chains to control the efficiency with which light and electrons can be transported by the polymer molecules.[6,7] One way to do this is to incorporate stable inorganic cross-linkers into conjugated organic polymer chains. Inorganic cross-linkers provide greater control of the alignment, stability, and electronic properties of organic polymer chains to form hybrid organic–inorganic structure materials. Hybrid organic–inorganic conducting polymers are ideal materials for organic electronics because they offer the structural flexibility and tunable optoelectronic properties of their organic components in addition to the stable and elegant electrical properties of inorganic components.[8–10]

In this study, we developed high-performance two-dimensional (2D) polydiacetylene with hybrid organic–inorganic structures using molecular layer deposition (MLD). MLD is a gas-phase layer-by-layer growth process, analogous to atomic layer deposition (ALD), that relies on sequential saturated surface reactions and results in the formation of an organic monolayer in each sequence.[11–17] We combined conjugated organic polymer layers with inorganic cross-linkers, to produce 2D polydiacetylenes. The inorganic layers constitute an extended structure bonded by powerful covalent interactions resulting in a high carrier mobility as well as good thermal and mechanical stabilities. The advantages of the MLD technique include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at low temperatures.[15] The construction of 2D polydiacetylene thin films can be accomplished with monolayer precision by ligand-exchange reactions of diethylzinc (DEZ) and hexadiyne diol (HDD) with UV polymerization, whereby the OH group on both ends of the diol sequentially react with the ethyl group of DEZ to produce bridging alkanes.[18,19] Zinc oxide cross-linked polydiacetylene (ZnOPDA) thin films may have enhanced carrier mobility or other favorable properties owing to their 2D structures.

Figure 1 shows a schematic outline for the present layer-by-layer synthesis of two-dimensional (2D) polydiacetylene films with zinc oxide cross-linkers. First, an ethyl zinc oxide monolayer was formed by exposing a substrate to the DEZ molecule in the MLD chamber. The DEZ molecule was chemisorbed on substrate surfaces rich in hydroxy groups through a ligand-exchange reaction to form C_2H_5ZnO species. Second, the ethyl group of the chemisorbed ethyl zinc molecule on substrates was replaced by an OH group of HDD with the living ethane to form a diacetylene layer. The OH group of the diacetylene layer provides an active site for the exchange reaction of the next DEZ molecule. Third, the diacetylene molecules were polymerized by UV irradiation to form a polydiacetylene layer. The zinc oxide cross-linked polydiacetylene (ZnOPDA) thin films were grown under vacuum by repeated sequential adsorptions of DEZ and HDD with UV polymerization. The expected monolayer thickness for the ideal model structure of ZnOPDA is about 6 Å.

In a true MLD process, the surface reactions must be self-terminating and complementary to yield a uniform, conformal, and high-quality polydiacetylene thin film. To verify that the surface reaction for HDD is indeed self-terminating, the dosing time was varied between 1 and 20 s. The growth rate of the ZnO-PDA films was measured by an ellipsometer at growth temperatures in the range 100–150 °C. The obtained film thickness per cycle for HDD became saturated when the dosing time exceeded 10 s (Figure 2a). This result indicates that HDD undergoes a self-terminating reaction with DEZ that is absorbed on Si substrates. Figure 2b shows that the growth rate as a function of the DEZ dosing time is quickly saturated when the pulse time exceeded 0.5 s. This result suggests that DEZ undergoes a fast self-terminating reaction with HDD adsorbed on the substrates. All the self-terminating growth experiments were performed over 100 cycles. The

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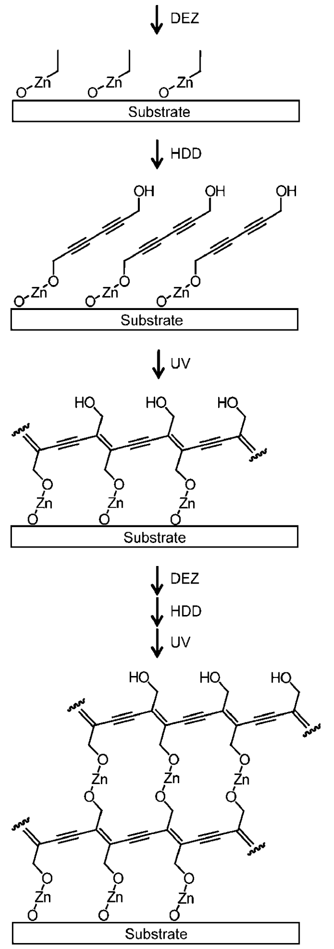

Figure 1. Procedure used to fabricate zinc oxide cross-linked polydiacetylene (ZnOPDA) thin films by molecular layer deposition.

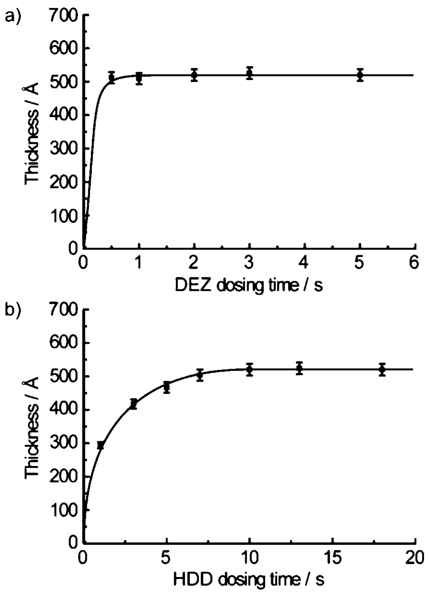

Figure 2. Thickness of the ZnOPDA films a) as a function of the HDD dosing time and b) as a function of the DEZ dosing time. All self-terminating growth experiments were performed over 100 cycles.

saturation data indicate that DEZ and HDD fully react with the active sites on the surfaces and that the reaction does not continue after saturation even though the precursors are present in excess.

The thicknesses of ZnOPDA thin films as a function of the number of MLD cycles were measured using cross-sectional transmission electron microscopy (TEM) (Figure 3 a).

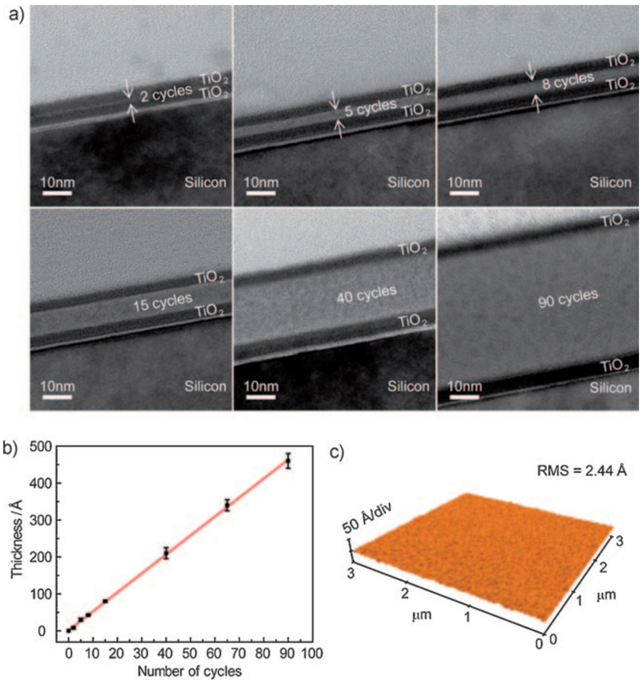

Figure 3. a) TEM images, b) thickness of the ZnOPDA films versus the number of MLD cycles, and c) AFM image of the ZnOPDA films.

These TEM images confirm the expectations for the monolayer thickness in the ZnOPDA films and the MLD growth rate. Figure 3 b shows that the polydiacetylene thickness increases nearly linearly as the number of cycles increases, indicating that the surface reaction for this MLD process are complementary and complete. The measured growth rate was about 5.2 Å per cycle, which is consistent with the ellipsometry results. The TEM images also show that the ZnOPDA films are amorphous and have no ZnO nanocrystals (Figure S1 in the Supporting Information). The AFM images of the ZnOPDA films showed very smooth and uniform surfaces, and the root mean square (RMS) roughness of the surfaces was as low as 2.5 Å (Figure 3 c). In comparison, the surface roughness of the initial cleaned Si substrate was about 2.1 Å. Regardless of the cycle number, the surfaces of the ZnOPDA films were as smooth as the initial cleaned Si substrate, indicating that MLD growth occurs in a 2D fashion through layer-by-layer growth. These results suggest that the MLD of the 2D polydiacetylene is self-limiting and proceeds by layer-by-layer growth, and that the MLD conditions are sufficient for complete reaction at temperatures of 100–150 °C. The thermal stability of the ZnOPDA films was studied by using TEM. The ZnOPDA films were stable in air up to temperatures of about 400 °C. This result, together with the ability of the 2D polydiacetylene to survive the TEM preparation process, confirms that polydiacetylene is covalently bonded by the zinc oxide cross-linkers.

Surface-enhanced Raman scattering (SERS) spectroscopy was applied to confirm the photopolymerization of the diacetylene thin films. A 100 nm thick Ag film was deposited on a Si (100) substrate by a vacuum evaporator. A 2 nm thick 2D polydiacetylene film was then grown on the Ag film. Ag nanoparticles with a diameter of 60 nm were dropped on the polydiacetylene surface under ambient conditions. Figure 4a illustrates a representative SERS spectrum for the ZnOPDA films sandwiched between the Ag nanoparticles and Ag film. Three Raman bands are clearly seen at $\nu_1 = 2127\ \text{cm}^{-1}$, $\nu_2 = 1525\ \text{cm}^{-1}$, and $\nu_3 = 1060\ \text{cm}^{-1}$, which are in reasonably good agreement with the previously observed Raman data for a polydiacetylene monolayer.[20] The narrow band at 2917 cm^{-1} is due to C–H vibrations. The prominent and broad bands around 1590 and 1360 cm^{-1} are similar to those observed upon irradiation of the excitation laser, which is interpreted to be a result of the conversion from polydiacetylenes into carbon materials, including graphite and amorphous carbon.[21] The SERS results indicate that diacetylene molecules in the films are polymerized by UV irradiation, which is in agreement with the generally known photopolymerization of diacetylene.

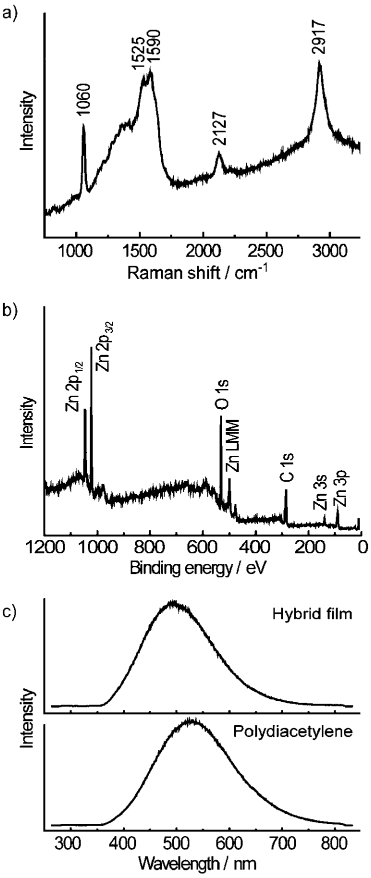

Figure 4. a) Raman spectrum and b) XP spectrum of the ZnOPDA film. c) Photoluminescence spectra of ZnOPDA and PDA films without cross-linkers.

X-ray photoelectron (XP) spectroscopic studies were performed to determine the composition of the ZnOPDA thin films grown by this MLD process. Figure 4b shows a survey spectrum of the 100 nm thick polydiacetylene thin film grown on a Si substrate. The XP spectrum displays the photoelectron and Auger electron peaks for zinc, oxygen, and carbon only. The peak area ratios for these elements, corrected by the elemental sensitivity factors, are 1:3.2:5.8 (Zn:O:C). As a comparison, the expected ratio from the model structure of the 2D polydiacetylenes (Figure 1) is 1:2:6. The higher oxygen atomic percentage could be explained by the adsorption of H_2O into the ZnOPDA films.[18] The water exists mostly on the surface of the films, since the O 1s peak decreases significantly relative to other peaks after Ar ion sputtering (Figure S2).

The photoluminescence (PL) spectrum of the ZnOPDA thin film is shown in Figure 4c. For the PL spectrum, the 100 nm thick polydiacetylene film deposited on the Si substrate was irradiated by a He–Cd laser ($\lambda = 325$ nm) as the excitation source. A broad peak near 500 nm is shown in Figure 4c. The PL spectrum indicates the possibility of using ZnOPDA films in optical devices involving electroluminescence. For comparison, a polydiacetylene (PDA) thin film without inorganic cross-linkers was also fabricated with a methanol solution of 2,4-hexadiyne-1,6-diol (HDD). A solution of 6 mM HDD in methanol was spin coated on a Si substrate at 1000 rpm for 1 min, and then the substrate was exposed to UV light for 10 min to form a 100 nm thick PDA film. The spectrum of the resulting film is very similar to that of ZnOPDA, but is shifted slightly toward long wavelengths (Figure 4c).[20]

To investigate the electrical properties of the 2D polydiacetylene thin films, we fabricated a thin film transistor (TFT) adopting a ZnOPDA film as an active layer. The TFT had a ZnO–PDA semiconducting channel grown on a 100 nm thick SiO_2/n$^+$-Si substrate at 100 °C, as shown in the device schematic in Figure 5a. The patterned Al source/drain electrodes were vapor-deposited on the ZnOPDA films using a shadow mask. As shown in Figure 5b, a typical output (drain current versus drain voltage: I_D–V_D) curve was obtained from the ZnOPDA TFT. The data indicate that ZnOPDA behaves as a n-type semiconductor. The maximum I_D level was around 40 µA under a 100 V gate bias. According to the transfer characteristics (I_D–V_G) shown in Figure 5c, a high field effect electron mobility of $> 1.3\ \text{cm}^2\text{V}^{-1}\text{s}$ was achieved in the saturation regime of $V_D = 100$ V along with an on/off ratio of greater than 10^6 and a threshold voltage of 45 V. The gate leakage current (I_G) was below 10^{-10} A. The device mobility obtained in this study is the highest among polydiacetylene-based TFTs. These ZnOPDA TFTs could increase the operating speed of flexible electronic devices. A TFT with a 30 nm thick PDA without cross-linkers was also fabricated and showed much lower field-effect mobility ($< 10^{-8}\ \text{cm}^2\text{V}^{-1}\text{s}$) than that of the ZnOPDA film (Figure S3).

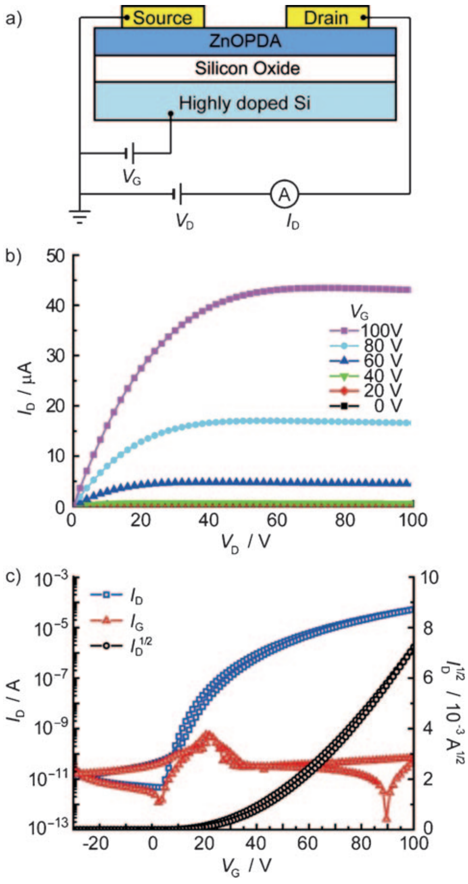

Figure 5. a) Diagram of the TFTs with a ZnOPDA active layer on highly doped Si substrates. b) Drain current–drain voltage (I_D–V_D) output curves of the TFTs. c) Drain current–gate voltage (I_D–V_G) transfer curves and the gate leakage levels of the TFTs.

In conclusion, we developed two-dimensional polydiacetylene with inorganic cross-linkers using MLD. The MLD process yields precision accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, and sharp interfaces at low temperatures. The fabricated ZnOPDA films exhibited good thermal and mechanical stabilities and an excellent field effect mobility ($>1.3\ cm^2V^{-1}s$). The MLD method is an ideal technique for fabrication of various 2D organic polymer thin films with inorganic cross-linkers and, furthermore, can be applied to fabricate organic polymer–inorganic hybrid superlattices.

Experimental Section

Materials**:** Unless otherwise noted, all commercial materials were obtained from Aldrich Chemical Co. and used without further purification. 2,4-Hexadiyne-1,6-diol (HDD) was obtained from Tokyo Chemical Industry and used as received. Deionized water was purified with a Millipore Milli Q plus system, distilled over $KMnO_4$, and then passed through a Millipore Simplicity system.

Preparation of substrates: The Si substrates used in this study were cut from p-type (100) wafers (LG Siltron) with resistivities in the range 1–5 Ω cm. The Si substrates were initially treated by a chemical cleaning process proposed by Ishizaka and Shiraki which involves degreasing, boiling in HNO_3, boiling in NH_3/H_2O (alkali treatment), boiling in HCl (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants and grow a thin protective oxide layer on the surfaces.[22]

Molecular layer deposition: The oxidized Si(100) substrates were introduced into a Cyclic 4000 MLD system (Genitech, Taejon, Korea). The zinc oxide cross-linked polydiacetylene (ZnOPDA) thin films were deposited onto the substrate using DEZ and HDD as precursors. Argon served as both a carrier and a purge gas. DEZ and HDD were evaporated at 20 and 80 °C, respectively. The cycle consisted of exposure to DEZ for 2 s, purging with Ar for 10 s, exposure to HDD for 10 s, and purging with Ar for 50 s. The total flow rate of Ar was 50 sccm. The deposited HDD layer was exposed to UV light ($\lambda = 254$ nm, 100 W) for 30 s. The ZnOPDA films were grown at temperatures of 100–150 °C under a pressure of 300 mTorr.

Sample characterization: Raman spectra were obtained by using a Raman spectrometer system (Renishaw Model 2000) equipped with an integral microscope (Olympus BH2-UMA). The 514.5 nm line from a 20 mW air-cooled Ar^+ laser (Melles-Griot Model 351MA520) was used as the excitation source. Raman scattering was detected with 180° geometry using a Peltier-cooled (−70 °C) charge-coupled device (CCD) camera. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. All XP spectra were recorded on a ThermoVG SIGMA PROBE spectrometer using an $Al_{K\alpha}$ source operating at 15 kV and 70 W. The binding energy scale was calibrated to 285 eV for the main C 1s peak. Each sample was analyzed at a 90° angle relative to the electron analyzer. The thicknesses of the polymer films were evaluated using an ellipsometer (AutoEL-II, Rudolph Research) and transmission electron microscopy (TEM; JEM2100F, JEOL). Current–voltage curves of the TFTs were measured by a semiconductor parameter analyzer (HP4155C, Agilent Technologies). The optical properties were measured by photoluminescence (PL) spectroscopy using a He-Cd laser (325 nm) in association with a spectrometer (Darsa, PSI Co. Ltd.).

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