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Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp657-658

Surface Manipulation of Precursor Carbazole Dendron Polymer Thin Films by Conducting-AFM Nanolithography

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1. Introduction

The manipulation of electrically conductive and semiconductive surface properties has been of considerable interest in nanometer scale electronic devices such as data storage memory devices and nanosensors. Various techniques of nanostructuring have been reported using atomic force microscopy (AFM) which includes: electrical nanolithography to fabricate a charged dielectric surface,[1] electrostatic nanolithography,[2] dip-pen nanolithography,[3] and electrochemical nanopatterning.[4] These techniques have been applied to fabricate conjugated polymer nanopatterns by direct electropolymerization[5] and by electrochemical conversion of an insulating precursor polymer to a conducting polymer via cross-linking.[6,7] In all cases, issues are mostly focused on the formation of nanopatterns and size-control as well.

Conducting polymers are widely studied polymers. These materials have received much attention due to their potential applications in light-emitting devices, field effect transistors, charge storage devices, photodiodes, sensors, resist materials, etc. Substituted poly(*N*-alkyl-3,6- carbazoles) are materials of great interest as they can act as hole transport materials when utilized in organic lightemitting diode (OLED) applications.[8] Electropolymerization of linear precursor polymers results in the formation of conjugated polymer networks and thin films primarily through inter- and intramolecular crosslinking reactions.[9] On the other hand, dendrimers are capable of forming individual conjugated polymer nanoparticles as well as being incorporated in thin film devices for sensor applications.[10]

In this study, conducting AFM nanolithography was used to manipulate the surface morphology of carbazole precursor dendron polymer thin films. Bias voltages were locally applied to the sample by using conducting AFM. We have successfully obtained the locally cross-linked conjugated polymer due to the polymerization (Cross-linking) and the doping of the polycarbazole.

2. Experimental

Figure 1 shows the structure of carbazole precursor dendron polymers used in this study. Au thin films were deposited on the glass substrate by a vacuum evaporation method and the precursor carbazole thin films were prepared by a spin-coating method. Figure 2 shows the schematic illustration of the AFM nanolithography. All the AFM nanolithography measurements were carried out in ambient air (relative humidity ∼40%) by using the vector scanning mode, in which the movement of the conducting AFM tip was able to be set by a program. First, the bias voltages were applied and processed to obtain dots or lines on the precursor thin film. Afterwards, the scale of the measured area was expanded to observe the change of surface morphology. In addition, the current-map image was observed using the conducting AFM, by which the electric conductivity in the raised morphology part was evaluated.

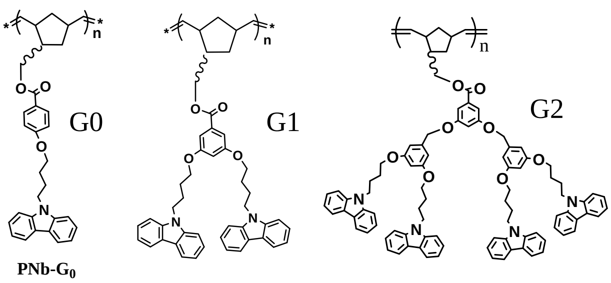

Figure 1. Carbazole Precursor Dendrons

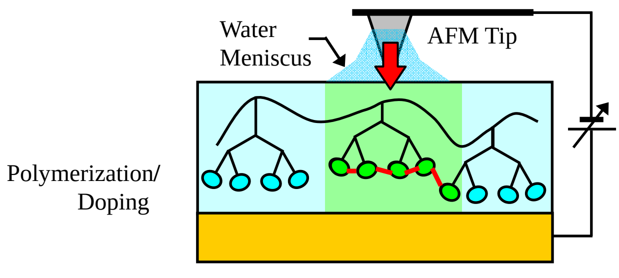

Figure 2. AFM nanolithography used in this study

3. Results and Discussions

Figure 3 shows the cross-linked/doped precursor polycarbazole film after the application of 5 V on the squared area. As shown in this Figure, the area of raised morphology was larger than the squared area, indicating the cross-linking/doping were generated outside the applied-voltage area. This should be attributed to electrochemical ion transport, which was assisted by water meniscus and residual mobile ions in the film. An increase in the height change of the film was observed as the applied voltage increased, while it decreased as scanning speed was increased.

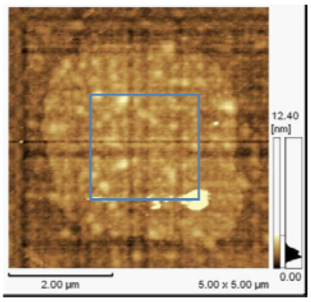

Figure 3. AFM height image of cross-linked/doped precursor polycarbazole film after the application of 5 V

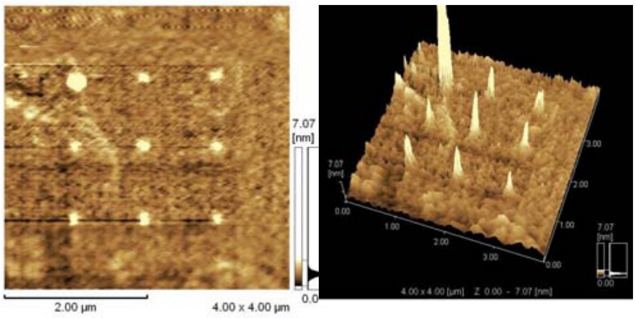

Figure 4. AFM height image after dots are processed by AFM nanolithography

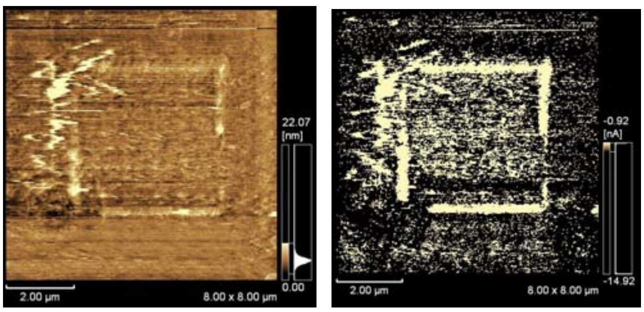

Figure 5. AFM height image and current-map image after the application of bias voltages

Figure 4 shows the AFM height image after applying at 5 V for 5 s at 9 points. As shown in this Figure, 9 dots structure on the precursor carbazole thin film was clearly observed after applying the bias voltage. Under ambient condition, a water meniscus is formed between the AFM tip and the film/substrate through capillary condensation. The dots can be fabricated because the ionic current flows through the water meniscus, generating the electropolymerization and the cross-linking of elecrtoactive pendant carbazole monomers present in the film.

Figure 5(a) and (b) shows the AFM height image after applying at 5 V, and the corresponding current-map image, respectively. In figure 5(a), the raised morphology in the area, where the line was drawn, was observed. In figure 5(b), the conductivity change on the raised morphology was observed. We believe that the increase of the conductivity was obtained by the bias processing because the ion such as the hydroxide ions (OH^-) in the water meniscus is doped in the electropolymerized polycarbazole dendron film. Moreover, it was confirmed that the humidity affected the change of the conductivity and dots structure formation because the water meniscus formation depends on the humidity.

3. Conclusions

In this study, AFM nanolithography using conductive probe was used to fabricate conjugated dendritic polymer nanopattern. The cross-linking for the nanoppatern was obtained at around 2-4 V. The different morphological change was obtained at different generation of precursor carbazole dendrimers. Applied voltage and writing speed dependences were also studied Furthermore, the increased current was observed by the electropolymerization.

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