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Effect of substrate surface on DR-19 films deposition process with using EFA-PVD method

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Abstract. The Disperse Red 19 (DR-19) with its conjugated chain structure is known to offer great potential for photonic device applications, such as optical switching and optical data storage. This researches aim to study surfactant effect of silane substrate and the effect of external electric field applied during the deposition process on properties of the resulted DR-19 film. This researches using Electric Field Assisted Physical Vapor Deposition (EFA-PVD) method. The characterization of the film structure was performed by means of XRD. The deposited molecular orientation was characterized with UV-Vis spectroscopic measurement. Based on these spectroscopic data, it is shown that anchoring mechanism with hydrogen bonding does occurred between DR-19 molecule and silane substrate responsible of the stability of the fabricated film. Result of this research show that DR-19 films have been obtained which exhibit crystalline structure with the molecules deposited in parallel polar orientation perpendicular to the silane substrate surface and regular head to tail stacking when increasing external electric field. This is understood to be result of the formation of strong hydrogen bonding acting as the anchoring mechanism.

1. Introduction

Azobenzene-based photoresponsive molecules such as Disperse Red-1, Disperse Red-19 and Disperse Orange-3 have been widely studied in solution. Disperse Red-19 (DR-19) polar molecule (4-N, N-di-(2-hydroxyethyl) amino-4'-nitroazobenzene) is an azobenzene-based molecule, known as a special group of molecules with a conjugated double-single bond chain structure. This molecule also known as a chromosphores which has high second order nonlinear optical microscopic (first hyperpolarisability), is related to its noncentrosymmetric structure (not having a center of symmetry). This molecule has been used as a nonlinear optical (NLO) chromosphores in the development of NLO and photorefractive polymer materials [1-4]. Organic thin films with good optical responsive properties have been produced and studied for potential applications in integrated optics such as optical switching, optical data storage and information processing [5-8].

Previous studies using the PVD (Physical Vapor Deposition) method showed that the deposition of the DR-19 molecule in the film was oriented perpendicular to the substrate surface in an antiparallel dipole arrangement. The same thing is also obtained that the DR-1 molecule is deposited with a regular arrangement of head-to-tail in a periodic structure along the molecular chain [9]. This is understandable because of the intermolecular dipole interactions, molecular deposition tends to aggregate as an indication in previous studies [10,11]. With this effect it is possible to influence the horizontal (lateral) direction structure of the deposited molecules. This is very useful to be studied in this research.

This researches aim to study surfactant effect of silane substrate and the effect of external electric field applied during the deposition process on properties of the resulted DR-19 film.

This researches using Electric Field Assisted Physical Vapor Deposition (EFA-PVD) method. The external electric field serves to orient molecules when they are deposited. The molecular deposition process is carried out by utilizing the interaction of the DR-19 molecule with the electric field (electric field-dipole interactions). In addition to electric field-dipole interactions, DR-19 intermolecular interactions (dipole-dipole interactions) also occur. These two interactions can occur because the DR-19 molecule has a large enough permanent dipole moment with respect to its noncentrosymmetric structure. The presence of dipole-dipole interactions causes the molecules to tend to be antiparallel oriented to other molecules, while electric field-dipole interactions cause oriented molecules in the direction of the field. By using an electric field to adjust the orientation of the molecular dipole, it can produce a molecular arrangement that is parallel and perpendicular to the substrate surface. The electric field used must be homogeneous so that the composition of the parallel molecules produced is evenly distributed on the surface of the substrate. For a parallel molecular arrangement to be maintained, a silane substrate (surfactant effect) is used because the DR-19 molecule can undergo hydrogen bonding with silane.

2. Experimental

2.1. Material
The material used in this study is the Disperse Red-19 (DR-19) molecular powder obtained commercially from Aldrich. DR-19 molecules have a molecular weight of 330.34 and a melting point of 300 C [12]. This molecule has a Donor-Bridge-Acceptor polar structure as shown in Figure 1.

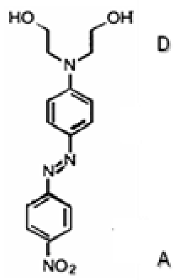

Figure 1. Molecular structure of Disperse Red-19

2.2. Film Preparation
In this study, DR-19 molecules were received in powder form and then processed in DR-19 film form. Samples in thin film form were deposited on silane substrate using VPC-410 vacuum evaporator from Ulvac Sinku Kiko, which was operated at pressure (2-4) x 10^{-5} torr. The substrate is placed 10 cm above crucible with the position of the stainless mesh electrode between the substrate and the crucible. The film is prepared with an external electric field variation of 0; 0.6; 1.9; 2.6 and 3.3 MV/m. The duration of thin film deposition is 1 hour. There is no additional treatment during the film deposition process.

2.3. Measurement
The Crystallinity or crystal structure was determined from X-ray diffraction (XRD) measurements with the PANalytical Diffractometer type operating on CuKα (α = 1,540598 angstrom) with X-ray sources at 40 KV and 30 mA. XRD measurements were obtained in a range of 2Θ from 3 to 40 degrees with step size 0.0167 degrees and time step 15.240 s. The deposited molecular orientation was characterized with ultra violet-visible (UV-Vis) spectroscopic measurement.

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3. Results and Discussion

The UV-Vis spectrum of the DR-19 film transmission mode with an external electric field variation is shown in Figure 2. It appears in Figure that an increase in the electric field causes a decrease in the absorption peak at the blue shift frequency. This phenomenon is an indication that the higher the electric field is given, the more molecules that sleep upright (vertically) are arranged to extend the chain upright along with the sleep aggregate contribution decreases.

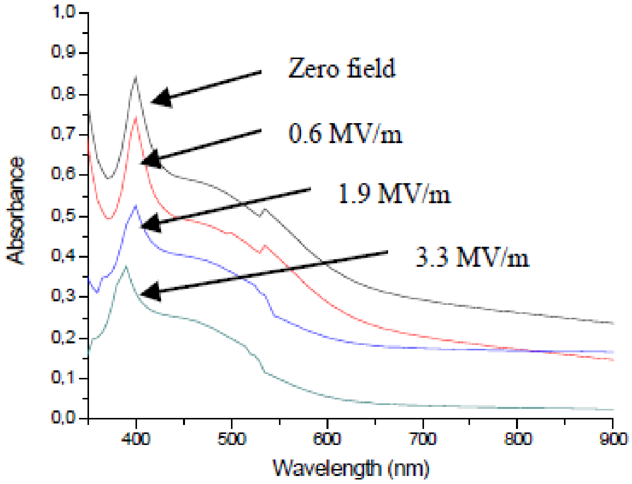

Figure 2. UV-Vis spectra of DR-19 film transmission mode for electric field variations

Figure 3 shows the spectrum of UV-Vis DR-19 film reflection modes with external electric field variations. The aggregation effect of DR-19 molecules in two directions (in plane and out-of-plane/ vertical) in the film deposited by the EFA-PVD method on the silane substrate surface. An increase in the electric field results in an increase in the absorption peak at the red shift frequency, indicating parallel aggregation. This phenomenon is an indication that the higher the electric field is given, the more molecules are arranged into parallel perpendicular to the silane substrate surface.

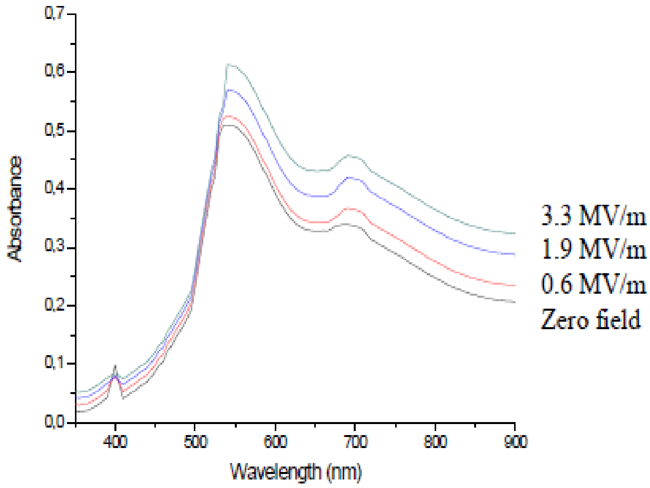

Figure 3. UV-Vis spectra of DR-19 film reflection mode for electric field variations

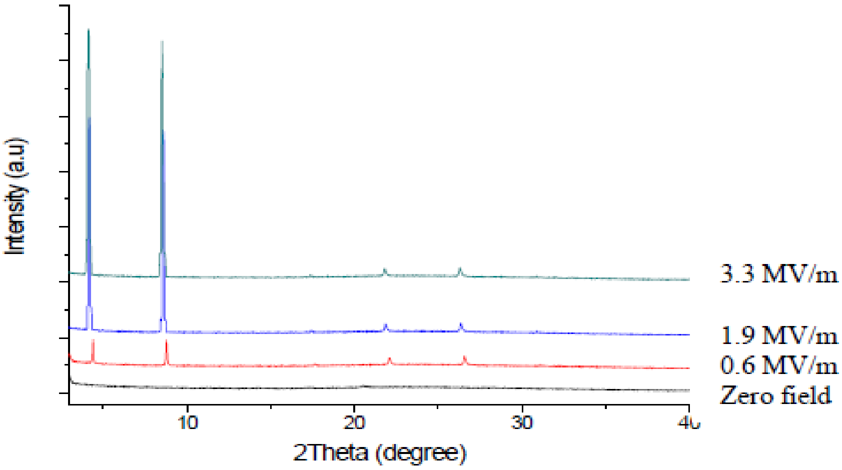

Figure 4. XRD spectra of DR-19 film on silane substrate for electric field variations

From Figure 4 show that there are two sharp peaks at 2θ = 4.2834° and 8.7884°. This result indicating that the DR-19 molecule is oriented perpendicular to the surface of the substrate with a head-tail configuration (stacking) with a periodicity of 20.60 angstrom for the first order peak and 10.05 angstrom for the second order. It also appears from the picture that there is an increase in diffraction peaks and sharper with an increase in electric field polling. This is indicate that there is an increase in crystallinity (the organization of the crystalline molecule) in films with an increase in the electric field [13], this is consistent with the spectroscopic analysis described earlier.

4. Conclusion

The deposition of DR-19 film using the EFA-PVD method shows good quality. Results of measurement analysis X-ray diffraction (XRD) shows that the DR-19 molecules are stacking perpendicular to the surface of the silane substrate, which shows an indication of the strong surfactant effect of the hydrogen bonding of DR-19 molecules with the silane substrate. Spectroscopic measurement results show that anchoring mechanism with hydrogen bonding does occurred between DR-19 molecule and silane substrate responsible of the stability of the fabricated film.

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