

# Influence of ITO Substrate Surface and External Electric Field to Improve DR-1 Film Refractive Index Using PVD Method

Donny R. Wenas, Marianus, Cyrke A. N. Bujung

**Abstract:** This research is aimed to study surfactant effect of ITO substrate and the effect of external electric field applied during the deposition process on properties of the resulted film. Further, the anchoring mechanism involved in the deposition of the molecule is investigated in relation with the properties of the fabricated film. In addition to that, the optical property of the film is also investigated to study the effect of the applied electric field.

For those purposes, a special electric field assisted Physical Vapor Deposition (PVD) method has been developed allowing the deposition process to be carried out under varied electric field. The deposited molecular structure and orientation were characterized with SEM, FTIR and UV-Vis spectroscopic measurement. Based on these spectroscopic data, it is shown that anchoring mechanism with hydrogen bonding does occurred between DR-1 molecule and ITO substrate responsible of the stability of the fabricated film. The refraction index of the film has been measured by means of reflectometer. The result of this research, DR-1 films have been obtained which exhibit crystalline structure with the molecules deposited in parallel polar orientation perpendicular to the substrate and regular head to tail stacking when the electric field applied larger than 0.59 MV/m. This is understood to be result of the formation of strong hydrogen bonding acting as the anchoring mechanism. In addition, it is shown that increasing external electric field leads to increasing refractive index of the DR-1 films corresponding to the number of DR-1 molecules deposited perpendicularly parallel to the ITO substrate surface is greater.

**Index Terms:** Keywords: Disperse Red-1, Surfactant Effect, Refractive Index, Hydrogen Bonding.

## I. INTRODUCTION

The study of organic material with conjugated single-double bond chain structure is interesting to study as a focus of research because this material is known as photonic material with a number of promising advantages, including a wealth of the structural of variations and molecular arrangement that can be adapted to the demands of a particular application. The material has a relatively fast and easy optical response made in the form of a device, so the cost is relatively cheaper. This material is the focus of the study because it has great potential for photonic applications such as electro-optical modulator, second harmonic generation

(SHG), directional coupler, optical switching, optical data storage and applications in integrated optical circuits which is useful for communication systems and optical information processing [1],[2].

Disperse Red-1 molecule (4-[N-ethyl-N-(2-hydroxyethyl) amino-4 '-nitroazobenzene) is known as a special group of molecules with conjugated chain structures. This DR-1 powder is red, has a molecular weight of 314.34, melting point 153°C and a thermal decomposition temperature of around 219°C [3]. This molecule is also known as a chromophore having second order nonlinear optical microscopic properties is high, related to its noncentrosymmetric structure (no center of symmetry), but even though the molecule is noncentrosymmetric, the second-order nonlinear optical of the crystal depends on the arrangement of the molecular dipoles. If the molecular dipoles are arranged in parallel polar orientation perpendicular to the substrate then the number of dipole moments becomes large and the film will have second-order nonlinear optical properties (SHG), but if the arrangement is antiparallel then second-order nonlinear optical properties will be lost and only third harmonic generation (THG) appears.

To meet the demands of applications in photonic technology, it is necessary to optimize optical properties and other supporting properties (optics, mechanical and thermal properties) through modification of organic responsive materials through modification of molecular structures and molecular arrangement. In addition, progress in the application of photonic devices is closely related to the development of quality thin film fabrication techniques because for such applications, the relevant responsive materials need to be processed in the form of thin films. The Disperse Red-1 (DR-1) molecule with its conjugated chain structure is known to offer great potential for photonic device applications, such as optical switching and optical data storage. For the aforementioned device applications, thin film of those molecules must be fabricated satisfying the requirements of having smooth and flat surface, uniform thickness and stable structure as well as attractive optical properties.

We present in this report the result of structural, the most favorable anchoring and aggregation effect of DR-1 films deposited on ITO substrate by PVD method under the influence external electric field, and the refractive index

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This research is aimed to study surfactant effect of ITO substrate and the effect of external electric field applied during the deposition process on properties of the resulted film. Further, the anchoring mechanism involved in the deposition of the molecule is investigated in relation with the properties of the fabricated film. In addition to that, the optical property of the DR-1 films is also investigated to study the effect of the applied electric field.

## II. LITERATURE REVIEW

One of the most used conjugated organic materials is DR-1. DR-1 Powder (4-[N-ethyl-N-(2-hydroxyethyl)] amino-4'-nitroazobenzene) now it can be obtained commercially. The material has a relatively fast optical response. This material is the focus of the study because it has great potential for photonic applications such as optical switching, optical data storage and applications in integrated optical circuits that are useful for communication systems and optical information processing [4].

The molecular structure of DR-1 is shown in Fig. 1, where this molecule consists of groups [N-ethyl-N-(2-hydroxyethyl)] amino as electron deficient, NO<sub>2</sub> as electron rich, and azobenzene groups that have conjugate bonds as  $\pi$ -electron bridges between the two groups. From this molecular structure it appears that the molecule has second-order nonlinear optical properties and has a permanent dipole moment in the direction of the chain because it is related to its noncentrosymmetric structure (no center of symmetry). But even though the molecule is noncentrosymmetric, second-order nonlinear optical properties of DR-1 do not automatically appear because it still has to be seen how the arrangement of the molecular dipoles in the crystal arrangement. If the molecular dipoles are arranged in parallel then the number of dipole moments becomes large and the film will have second-order nonlinear optical properties, but if the arrangement is antiparallel then second-order nonlinear optical properties (SHG) will be lost.

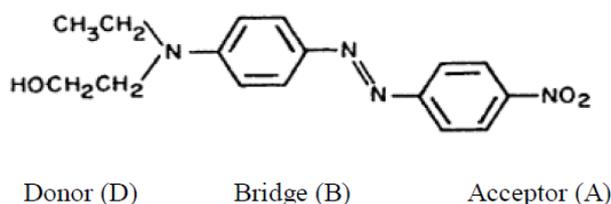


Fig. 1. Molecular structure of DR-1

For the development of nonlinear optical polymer materials, the DR-1 molecule has been used as a second-order nonlinear optical chromophore in host-guest systems [5]. In this system, DR-1 (guest) material is dissolved into a polymer matrix (host) such as poly styrene sulfonic acid (PSSA) without covalent bonds between the two components of the material, but is only bound by electrostatic forces such as hydrogen bonds or Van der Waals bonds. However, nonlinear optical polymer materials with this system have disadvantages associated with low nonlinear

optical chromophore concentrations because they are limited by the aggregation effect. Besides the host-guest system, it is also known as a side-chain system [6]. In this system, nonlinear optical polymer films have higher properties compared to guest-host systems due to an increase in the DR-1 chromophore in the film, but the levels remain limited.

Progress in the application of photonic devices with nonlinear and photorefractive optical materials is closely related to the development of quality thin film fabrication techniques because for such applications, the responsive materials need to be processed in the form of thin films. Film deposition processes, may not cause damage or change in molecular structure. The resulting film must have a flat, smooth surface, homogeneous thickness and high purity. In addition, the film formed must have optical transparency, thermal stability and good mechanical strength.

Research by thin films using electric fields was carried out by Hu et al [7], but the study was limited to the influence of the electric field on changes in the chemical environment of Cu (copper), the results showed that the electric field could change the chemical environment of Cu and increase the molecular order of CuPc (copper phthalocyanine). Another study was conducted by Sakai et al [8] which examined the FETs (field effect transistors) of CuPc films using cylinder furnaces. Current and voltage are observed in the FET characteristics of CuPc films. The results were obtained that orientation assisted by electric fields was effective in the sub millimeter region.

Both of the above studies use electric fields but for studies that are different from those carried out in this study. This study examines the anchoring mechanism of polar molecules deposited on the ITO substrate due to the influence of the external electric field, the effect of the surfactant effect (substrate surface) in its anchoring mechanism, the orientation of the molecules arranged parallel perpendicular to the substrate and the influence of the electric field in controlling optical properties film (refractive index).

## III. METHODOLOGY / MATERIALS

The DR-1 (4-[N-ethyl-N-(2-hydroxyethyl)] amino-4'-nitroazobenzene) powder used in this experiment was obtained commercially from Aldrich. The molecule has a formula weight of 314.34, a melting point of 153 °C with the onset temperature of thermal decomposition at 219 °C as determined by TGA measurement [3]. This molecule has the Donor Bridge Acceptor polar structure as shown in Fig. 1.

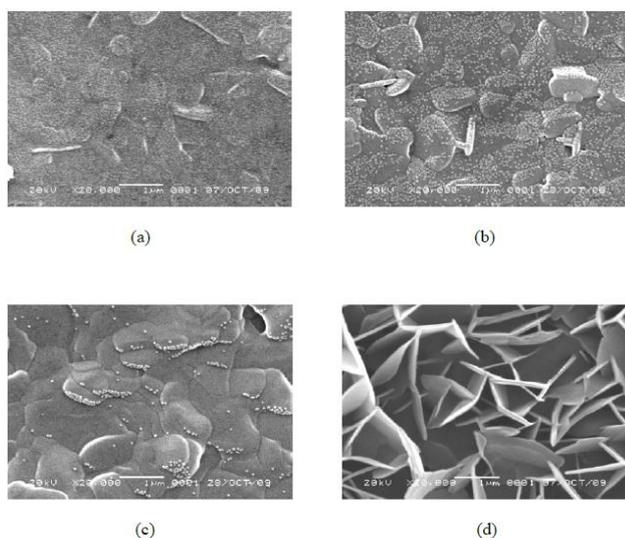
Samples in the form of thin films were deposited on an ITO substrates using VPC 410 Vacuum Evaporator from Ulvac Sinku Kiko, which was operated at about (2-4) x 10<sup>-5</sup> torr, with crucible temperature at 168 °C and substrate temperature at 26 °C. The ITO substrate also acts as a counter electrode for the generation of the electric poling field. It was placed at about 10 cm above the crucible with a stainless steel mesh electrode. The films were prepared with various external electric field strengths of 0 until 3.3 MV/m. The duration of the deposition process of all the thin films was about 1 hour. No further treatment was performed on

the deposited films.

The micro structure of DR-1 films obtained with SEM-EDX (SEC, SNE-4500). Characterization of structure and molecular orientation used by RAS-FTIR Perkin Elmer and UV-Vis Spectrometer Lambda 35 Perkin Elmer. Measurements of the refractive index and film thickness were carried out using the NanoCalc-2000 VIS Reflectometer.

#### IV. RESULTS AND FINDINGS

The SEM images of DR-1 films as deposited on ITO substrate for various electric fields as depicted Fig. 2. This figure shows that for zero fields, many DR-1 molecules that sleep in an irregular direction (amorphous) cover a part of the pattern of the molecular crystal plane and the crystal pattern is still not dominant. For the 0.59 MV/m electric field, the crystalline plane pattern has begun, the aggregates of the sleeping molecules have begun to be arranged perpendicular to the substrate, but still not dominant. For the 1.9 MV/m electric field, the pattern of the crystalline plane is more visible and the aggregate of DR-1 molecules that sleep regularly arranged perpendicular to the ITO substrate has begun to appear, although there are still many aggregates of DR-1 molecules that are still sleeping. In a large electric field of 3.3 MV/m, it is clear that the aggregates of DR-1 molecules are arranged regularly perpendicular to the ITO substrate surface forming patterns of the crystal plane in a three-dimensional direction.

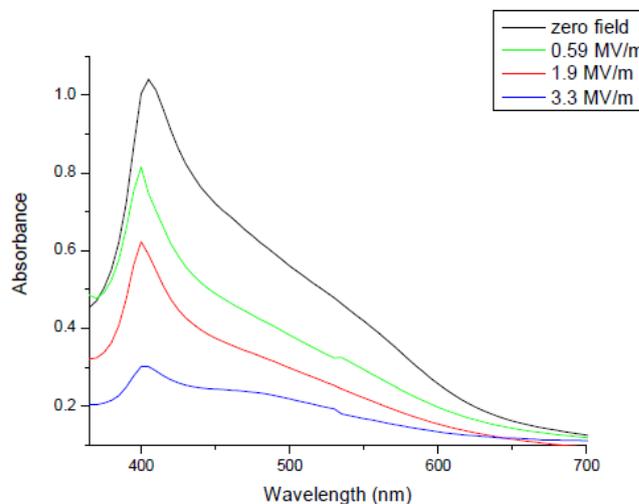


**Fig. 2.** SEM images of DR-1 films as deposited on ITO substrate for various electric fields

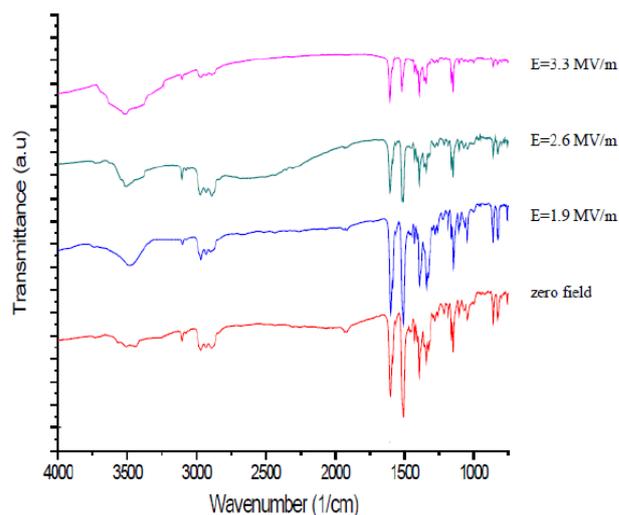
(a) zero field, (b)  $E=0.59$  MV/m, (c)  $E=1.9$  MV/m, (d)  $E=3.3$  MV/m.

Fig. 3, shows the aggregation effects of DR-1 molecules lying in the films deposited by PVD under influence of electric field with ITO substrate which are observed by UV-Vis spectroscopic measurements. This figure shows that the maximum absorption at 407 nm was obtained from the film sample deposited in zero fields, which is associated with the anti-parallel molecular arrangement. Increasing the electric field leads to decreasing absorption peak at blue

shifted frequency of anti-parallel aggregate, while retaining the single molecule absorption which decreases at lower pace in conjunction with increasing number of vertically deposited molecule [9].



**Fig. 3.** UV-Visible absorption spectra of the DR-1 films for various external electric fields



**Fig. 4.** FTIR spectrum of DR-1 films for various external electric fields

The RAS-FTIR spectrum of DR-1 films for various external electric fields as deposited on ITO substrate are shown in Fig. 4. From the picture it appears that with an increase in the electric field an increase in the absorption band of hydrogen bonding is enlarged and widened ( $3520\text{ cm}^{-1}$ ). This figures indicates that increasing the electric fields leads to decreasing absorption peak, as clearly seen at  $1606\text{ cm}^{-1}$  (C=C stretching skeletal),  $1517\text{ cm}^{-1}$  ( $\text{NO}_2$  asymmetric stretching),  $1406\text{ cm}^{-1}$  (N=N stretching), and  $1147\text{ cm}^{-1}$  (C-N stretching). All these absorption bands are associated with the dipole oscillations along the long molecular axis, as shown in Table 1. The absorption band associated with the dipole oscillation along the axis of the molecular length (body) decreases, and absorption on the surface of the substrate increases. This means that



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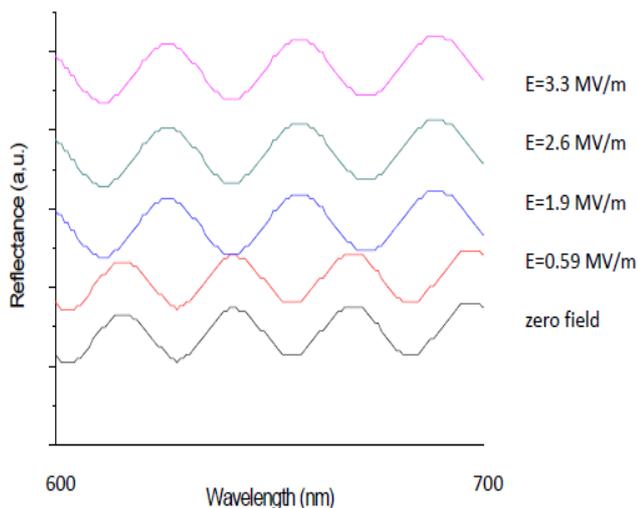
with the increase in the electric field, the number of DR-1 molecules deposited perpendicularly parallel to the ITO substrate surface is greater, this is indicated by the increase of hydrogen bonding absorption bands on the surface of the substrate [10]. This observation clearly support the previous suggestion that molecules deposited perpendicular to the substrate and coupled in parallel configuration in the film.

**Table I.** Identification of the main absorption peaks in FTIR spectrum of DR-1 film

Frequency (cm <sup>-1</sup> )	Mode assignment [11]
3520	Hydrogen bonding
1606	C=C stretching in skeletal
1517	NO <sub>2</sub> asymmetric stretching
1406	N=N stretching
1392	NO <sub>2</sub> symmetric stretching
1147	C-N stretching of aliphatic amine
860	C-H (out-of-plane bending) nearby NO <sub>2</sub>
829	C-H (out-of-plane bending) of aromatic

The direction of each vibration mode denoted in the last column refers to the long molecular axis (c-axis).

The optical properties of the film were measured by a reflectometer (NanoCalc-2000 VIS) to assess the effect of the external electric field used in the deposition process of the DR-1 film on the ITO substrate surface. Measurement results from samples obtained with different fields in the range of wavelengths from 600 nm to 700 nm, are shown in Fig. 5. Each measurement of the DR-1 film sample, always begins with the measurement of the substrate without the DR-1 film as a measurement reference that aims to eliminate the background effect from the data shown in Fig. 5.



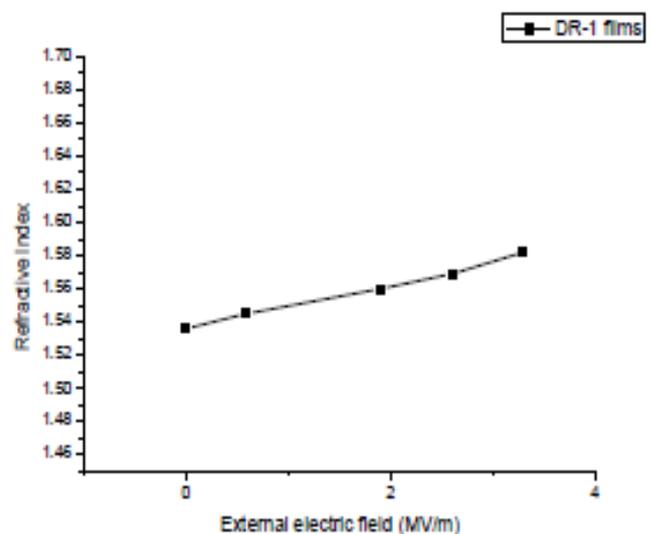
**Fig. 5.** The results of DR-1 film reflectometer measurements were deposited on the ITO substrate for external electric field variations in the wavelength range (600 - 700 nm).

The results of the fittings for determining the refractive index of the DR-1 films are based on reflectometric data with the ITO refractive index  $n_2 = 1.800$ ; ITO thickness  $d_2 = 4000$  nm is shown in Table 2.

**Table II.** Results of the fittings for determining the refractive index of DR-1 films

Electric Field (MV/m)	Refractive Index of DR-1 films
0	1.536
0.59	1.545
1.9	1.560
2.6	1.569
3.3	1.582

Based on Table 2, a graph of the refractive index (n) is made as a function of the electric field in Fig. 6. From the results presented in Fig. 6, there appears to be an increase in the value of the refractive index (n) monotonically with an increase in the electric field applied in the deposition process. This is thought to be due to the increased concentration of DR-1 molecules which are regularly deposited perpendicular to the ITO substrate in the film with an increase in the electric field.



**Fig. 6.** Refractive index of DR-1 film as a function of the external electric field

## V. CONCLUSION

The SEM image recordings show that with the help of the external electric field, the resulting film shows an orderly structure which increases with the formation of a crystalline structure in the film on the surface of about 3.3 MV/m. RAS-FTIR data analysis shows the occurrence of hydrogen bonding between DR-1 molecules deposited with ITO substrates. Furthermore, analysis of UV-VIS spectroscopy shows that the molecule is deposited in a parallel direction perpendicular to the ITO substrate surface. This result supports the stability of film structure thanks to a strong anchoring mechanism. Reflectometer measurements on DR-1 films show an increase in the optical refractive index as a result of an increase in the external electric field in the deposition process of the DR-1 films.

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