

# Analysis of mechanisms responsible for the formation of dark spots in organic light emitting diodes (OLEDs): A review

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## ABSTRACT

Organic Light Emitting Diode (OLED) is a new promising technology in lighting and display applications due to the advantages offered by the organic over inorganic materials. Nevertheless, the devices poor environmental stability and growth of dark spots has been a major concern for OLED devices. Based on the past literatures, several failure mechanisms have been proposed, suggesting that there is no particular model for the mechanisms of dark spots formation. In addition, the formation of dark spots is relatively obscure and unpredictable. On top of that, comprehensive reviews on the dark spots formation mechanism and the prevention methods are very limited at the current moment. Yet, both information are truly critical to be obtained and understood for OLED future development works. Thus, this paper reviewed particularly on the root cause formation of dark spots mechanisms in OLED devices. The dark spots are mainly formed due to the presence of foreign impurities and pinholes, as well as due to high current intensity. These root factor of elements will further enhance the degradation of OLED via bubble formations, electro-migrations, crystallizations and many other damaging processes. A few prevention steps have been discussed in order to reduce and prevent the dark spots from occurring such as the proper material selection and conducting the fabrication process in a controlled environment.

## 1. Introduction

Energy-saving issues have always been highlighted extensively in order to reduce the global warming effects due to greenhouse gases emission, especially in lighting applications [1–5]. According to the United Nations Environment Program (UNEP), the electricity consumed for lighting purpose is almost 20% across the globe [6]. In fact, almost 30% of the total carbon dioxide (CO<sub>2</sub>) emissions are associated with electrical power production, of which virtually half of the total productions are used up for lighting purpose [7]. Corresponding to this event, the energy generated is nearly 6% of the world's greenhouse gasses which is equivalent to 70% of CO<sub>2</sub> emissions or approximately 1.9 billion tons of CO<sub>2</sub> engendered from all vehicles worldwide [8,9].

In addition, Powell et al. also stated that more than 2650 billion kilowatt-hour (kWh) is generated for over 30 billion operating lamps around the world per annum which resulted in more than 1.5 billion tons of greenhouse gasses produced in a year [9]. Powell and his co-researchers also added that research and development (R&D) efforts for high-efficiency lighting applications are needed to be performed,

especially from both universities and industries as the demands of those products has become a real deal.

By considering this matter seriously, United Nations has declared the year 2015 as the International Year of Light and Light-based Technologies (UN-IYL), so that the issues of sustainability and development towards the energy-saving products such as organic light emitting diodes (OLEDs) will be the major prominence. In brief, changes in lighting can have a large impact on world's energy consumption, carbon footprint and environmental effects as lighting account for more than 19% of all electrical energy production globally [10].

Thus, this paper intended to describe and discuss the mechanisms analysis that responsible for the formation of dark spots in OLEDs. Moreover, a few prevention steps to reduce or prevent such deleterious effects for OLED technology are reported as well. Understanding and controlling the dark spots in OLEDs is a very important issue in terms of solving the problem of long lifetime and stability of OLEDs. In addition, a brief description on the OLED technology is also presented as an overview in understanding this high-end technology.

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## 2. Background on OLEDs technology

As the name suggests – OLED is made up of organic compounds (carbon-based materials). In current years, research areas and novel applications focusing on OLED have been rapidly developed [11–14], making OLED as a rising and promising high-end technology for practical applications in illumination field due to the advantages offered by organic over inorganic materials. They are including high brightness and contrast, high luminous efficiency, good chemical compatibility, relatively easy to operate, super thin, low heat dissipation, fast response time, wide viewing angle, low power consumptions, lightweight, as well as easier and simpler manufacturing process [15–19].

Although the first organic electroluminescence which has been discovered in 1963 by Pope et al. is now more than 50 years old [20], the invention of contemporary OLED is only about half of that age, when Tang and vanSlyke demonstrated the first high-efficiency device in 1987 at Eastman Kodak [21]. One groundbreaking aspect of their study of OLED was the construction of two amorphous organic semi-conductors. The organic materials were chosen in a specific way to confine the recombination of the majority of injected carriers to the heterojunction region and away from the electrodes. Nowadays, OLED has received considerable attention from both OLED communities and lighting manufacturers worldwide.

### 2.1. OLED structure and operating mechanism

Basically, an OLED is made up of several layers that composed organic matters, sandwiched between two electrodes, anode and cathode [22,23]. It can be designed to emit a single color of light, white light or even tunable colors. OLED utilizes the principle of electroluminescent [24], where a visible light will be emitted by the compound of materials used in response to the electric current or voltage applied [25–27].

Generally, an OLED's structures may differ from one to another, depends on its application. There are three types of structures commonly fabricated [28,29]. They are single-layer (the most basic structure), double-layers and three- or multi-layers of OLED. Most of the time, however, an OLED consists of six rudimentary structures [28–30] in order to improve the device efficiency and to reduce the water vapor transmission rate (WVTR) into the OLED. The structure basically consists of cathode, electron transport layer (ETL), light emissive layer (EML), conductive layer or hole transport layer (HTL), anode and substrate as shown schematically in Fig. 1. In order to enhance the conductive properties, the materials of ETL, EML and HTL may be varied accordingly. In this way, a more constant electrical profile [31] which lead to the fully used charge and impede a charge from reaching the opposite terminal [32] can be wholly achieved.

Fundamentally, as voltage is applied and current started to flow, electrons will move from cathode to anode. Thus, the electrons will be injected into the ETL at the cathode terminal (where ETL's function is to transport electrons to EML). At the same time, the electrons are withdrawn from the anode contact. This condition can also be described as

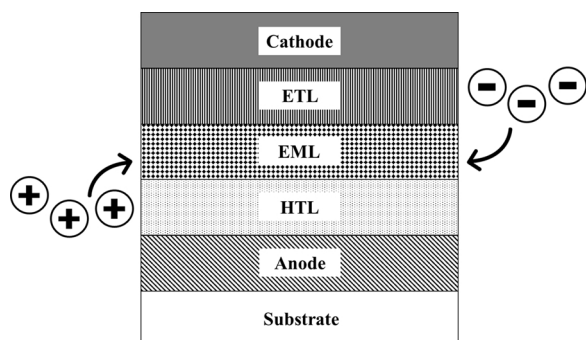


Fig. 1. Typical OLED's structure (multi-layers).

the injection of electron holes into the HTL. Later, the ETL will become rich in negatively charged electrons, whereas the HTL will be loaded with positively charged holes. Eventually, when a hole meets and combines with an electron due to electrostatic forces, the two things will be cancelled out and released a momentary burst of energy in the form of a visible light particle known as photon [33] within the emissive layer as holes are more mobile than electrons in organic semi-conductors. This basic working principle of an OLED is also depicted Fig. 1.

The organic materials of an OLED can be either polymeric or composed of small molecules and may include inorganic components. Meanwhile, the electrodes may consist of metals, metal oxides, carbon nanomaterials or any other possible species [34]. The completed organic layer has a thickness on the order of hundreds of nanometers or less than 1/1000 the diameter of a hair [35]. Furthermore, unlike LED, an OLED produces light that has no glare and is gentle to the eyes where the light is diffuse into large-area [30,34]. It is because the energy is applied uniformly over a large area, making the temperature rise during operation is small. Thus, an OLED does not have the heat dissipation problem that frequently afflicting inorganic LEDs.

### 3. Root cause formation of dark spots mechanisms

Even though OLED is envisaged as a new promising technology for energy-efficient in lighting and display applications due to abundant of advantageous offered, it still suffers from degradation processes. Most of the time, the impairment of an OLED is frequently attributed to the formation of a local non-emissive area or known as dark spots, created on the OLED's surface which will cause further damage and lead to a total malfunction of the OLED systems. Typically, the formation of dark spots is associated with the presence of humidity, moisture and impurities, as well as high electric current supply [36–44]. The humidity and moisture can be diffused through an OLED's film by various factors such as film structure, film permeability, film thickness, film area, temperatures and pressure across the film [45].

Based on the past studies, several failure mechanisms have been proposed, suggesting that there is no exact and ultimate answer for the root cause of dark spots formation that indicated the deterioration of an OLED. However, from the reviews done, two main root causes are noticed. They are (1) presence of foreign impurities and pinholes and (2) due to high electric current intensity.

#### 3.1. Presence of foreign impurities and pinholes

McElvain et al. [46] have conducted a research on the formation and growth of dark spots in OLED samples at ambient conditions and under low electrical stress. The OLEDs consist of indium tin oxide (ITO), *N,N'*-diphenyl-*N,N'*-bis-(3-methylphenyl)-{1,1'biphenyl}-4,4'-diamine (TPD), tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>), magnesium (Mg) and silver (Ag) which can be denoted as ITO/TPD/Alq<sub>3</sub>/Mg/Ag for simplification. The OLEDs have been tested at varies stress time (2 min/10 h/20 h/30 h/40 h) with a constant voltage of 4.5 V. The results found that the area of dark spots is increased linearly with the stress time. Gradually, the dark spots' diameter becomes larger and will be combined with each other to form even a greater circular shape on the OLED samples. On the other hand, the number of dark spots are remained the same and do not evolve with time.

The authors suggested that there are two factors that influenced the luminance performance of OLED devices. The first factor would be the reduction of electrical current flow into the OLED samples due to the increment of an internal resistance. It is found that the OLED's luminance is immensely decelerated after operating in the first 10 h and continuously decreased at a much slower rate for the following operating hours. In this particular experiment, however, the severe luminance performance is found to be independent of the formation of dark spots, since the OLED samples are tested under dry nitrogen

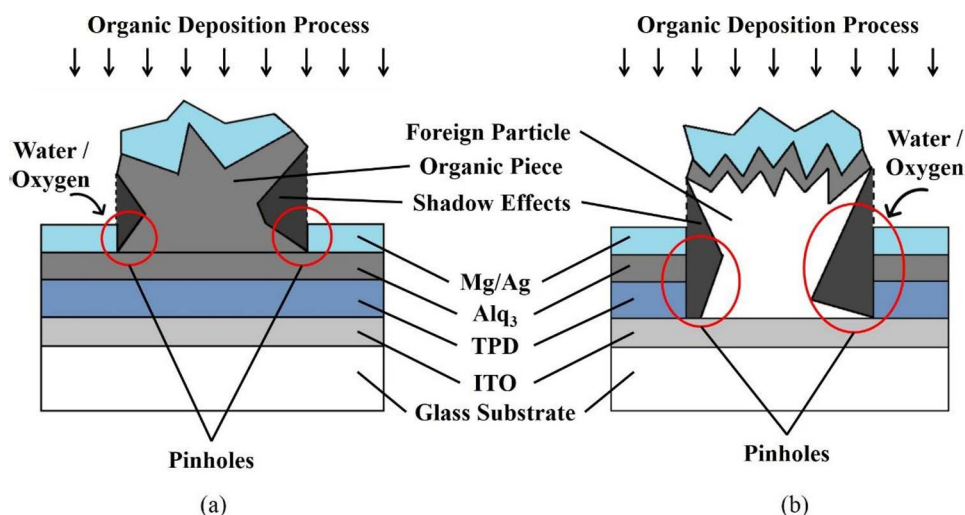


Fig. 2. Shadow effects on OLED's surface due to: (a) organic piece spluttered during organic deposition process and (b) presence of impurities before organic deposition process.

surroundings. This is because dark spots could not emerge in such conditions. Thus, the authors suggested that there is a proportional relationship between the luminance performance and quantum efficiency of the devices.

The next factor that affected the luminance action of OLEDs is due to the reduction of an active emitting area which is correlated with the formation of non-emissive areas or dark spots. According to McElvain and his co-workers, pinholes are detected on the OLED's surface which might be introduced by, first, the organic pieces during the organic deposition process (Fig. 2(a)). During the process, organic pieces might be deposited due to the "sputtering" of the organic material. Secondly, foreign particles or any other impurities could have been embedded on the device's surface before the deposition process takes place due to the contaminated surroundings as depicted in Fig. 2(b). According to the authors, all these impurities will cause shadow effects during the deposition position. This event would be possible if the size of the particles is bigger than the thickness of organic layers (TPD/Alq<sub>3</sub>) as illustrated in Fig. 2(a) and (b).

Due to the shadow effects, tiny pinholes are created. These pinholes will further allow the infiltration of water and oxygen into the OLEDs with respect to the incomplete coverage layer. Eventually, oxidation process will occur as the water or oxygen is able to penetrate through the tiny pinholes as described in Fig. 3 before. This oxidation process will result in the alteration of volumetric constituents around the pinhole areas. As an outcome, adhesion between the electrode layer (Mg/Ag) and the interface of organic layer (Alq<sub>3</sub>) become weaker and induce the delamination process. Once the delamination process occurs, it will

cause the formation of dark spots since the electrons cannot be injected into the organic layer. The authors believed that the injection paths of electrons may be impeded by the delamination action between the two layers. In this paper, however, the authors do not lucidly describe the mechanisms on how the oxidation process is taking place within the layers of the OLED device which causes the delamination to take place.

Agreed with the previous research done by McElvain et al., Aziz et al. [47] also believed that the presence of pinholes is the main reason lead to the dark spots formation. This is due to the fact that those pinholes provide pathways for humidity to penetrate into the OLEDs. This presence of humidity or water is capable of causing destruction in the structure layers of OLEDs. In addition, the authors also added that the humidity may be introduced by the presence of residual moisture in an organic layer itself. This may promote further degradation processes even for the encapsulated OLEDs.

Aziz and his co-workers have discovered crystalline cluster regions on the top of Alq<sub>3</sub> surface layer. The regions are confirmed to be an accumulated mass of Alq<sub>3</sub> by using microscopic infrared (IR) spectroscopy. It means that there are no other new chemical species formed on the cluster regions, but Alq<sub>3</sub>. The Alq<sub>3</sub> surface layer is revealed to be changed from the amorphous film into the crystalline structures due to Alq<sub>3</sub> hydration that leads to a device failure. The IR absorption spectrum of a crystalline cluster verified that the region holds a higher water content and water/Alq<sub>3</sub> ratio as compared to the vicinity of amorphous regions.

The authors also pointed out that the crystalline clusters will grow in size by time. As the clusters will become larger, thicker and denser

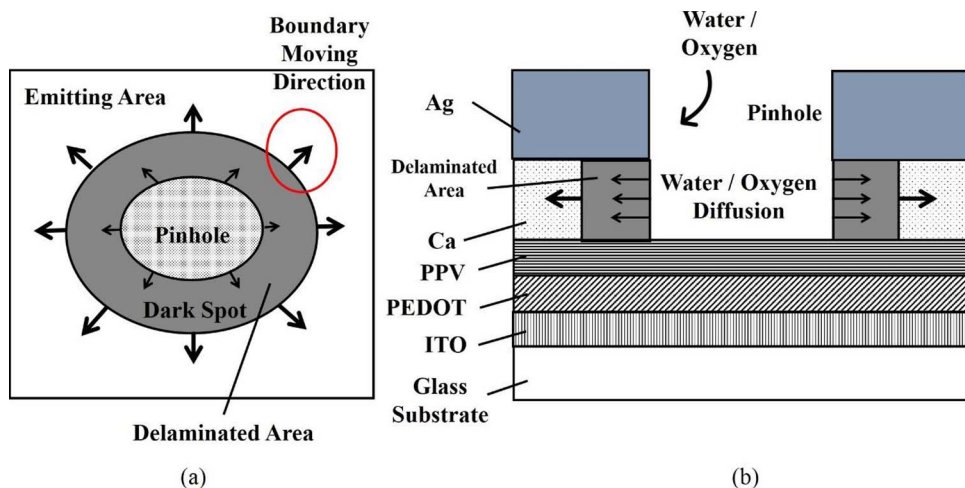


Fig. 3. Proposed mechanism of dark spot growth: (a) top view and (b) side view of OLED devices.

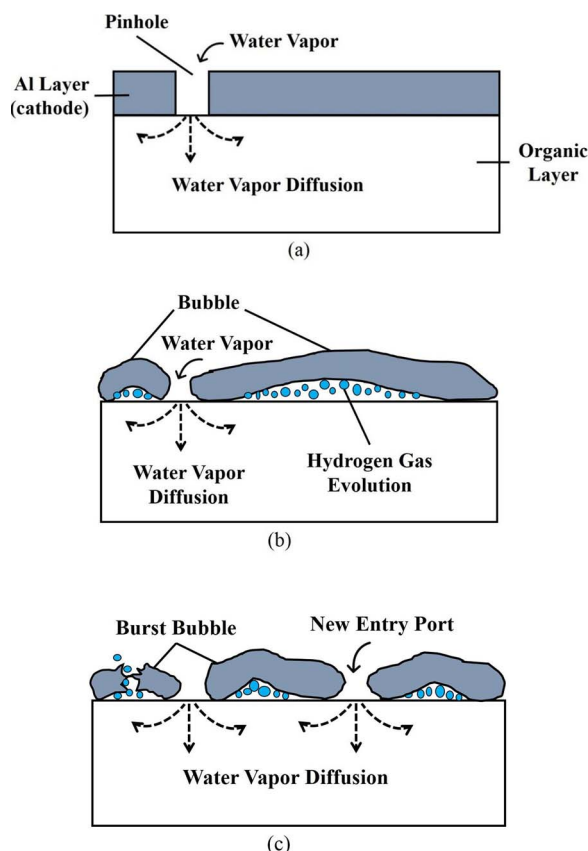


Fig. 4. Process of dark spot growth: (a) presence of pinhole allow the penetration of water vapor, (b) bubbles formation due to hydrogen gas evolution, and (c) burst bubbles provide extra entry ports for water vapor penetration.

than the surrounding regions, they will eventually lift-up the cathode layer and thus form cathode domelike shapes. Ultimately, that particular area will become a non-emissive spot, and hence, a dark spot is formed. This is due to the detachment of contact between the cathode and organic interface where electrons movement are hindered. Hence, Aziz et al. implied that humidity is the main reason which induced the crystallization in the  $\text{Alq}_3$  layer and leads to cathode delamination which will finally produce dark spots.

Four years later, Lim et al. [48] also proposed that the root cause of dark spots formation in OLEDs is due to the presence of dust particles which will initiate the additional processes that lead to OLED's failure. Based on their discussion, the authors said that these dust particles could have been introduced during the OLED fabrication. The apparent difference between the proposed mechanisms of dark spots growth between McElvain et al. and Lim et al. is that, McElvain et al. believed the delamination of electrode will only arise after the oxidation process, whereas Lim et al. suggested that delamination of electrode and oxidation processes take place at the same time.

In their study, Lim and his co-researchers have demonstrated the dark spot growth in multi-layered OLED (ITO/polyethylenedioxythiophene (PEDOT)/poly (*p*-phenylene vinylene) (PPV)/calcium (Ca)/Ag) by controlling the pinhole sizes and shapes. In this particular experiment, there are two types of pinholes (type A and type B) formed on the OLED samples. For type A, the pinholes are made by inserting tiny silica spheres with diameters ranging from 1.00, 2.01 and 4.00 to 5.99  $\mu\text{m}$  into the OLED samples. Since the total thickness of the samples is less than 400 nm, the silica spheres had caused a shadow effect on top of the surface which inhibits a smooth and complete cover of Ca and Ag layers, hence pinholes are created.

Meanwhile, for type B, the pinholes are created without the silica spheres. A few miniature holes about 4  $\mu\text{m}$  are produced by compacting

the silica spheres into OLED samples by using compressed nitrogen. The authors noticed that the dark spots with inserted silica spheres are consistently distributed with same magnitudes. On the other hand, dark spots without the silica spheres comprised larger distributions with disseminated sizes and shapes. The statistical results proved that the distribution area of dark spots obtained is corresponding with the Gauss function which is parallel with the occasion of normal dust distribution. Thus, Lim et al. proposed that the presence of the foreign substance is a significant reason for the formation of a pinhole. Accordingly, the authors have suggested a mechanism of dark spot growth as shown in Fig. 3.

Water and oxygen are able to pass through the sample via the pinholes created by the presence of dust particles. Ultimately, delamination process will occur between the interface of the cathode and organic deposits. At the same time, the oxidation will also take place in some parts of the cathode active metal. The combination of these two processes can cause the electron injection to be stopped from the cathode into the organic layer in which causing that area to become dark during operational of the device.

As proposed by Lim et al., there is a circular boundary-shaped which is formed between the delaminated (denoted with dark grey color) and non-laminated areas as indicated in Fig. 3. The delaminated region is increased proportionally with time as water and oxygen are perforated through the wall of pinhole which causes further delamination and oxidation process at the boundary sideways. Meanwhile, the growth of dark spots is determined by the flow rate of water and oxygen that penetrated into the OLED samples.

Schaer et al. [49] also have established a similar result with the two studies as discussed before, where the key factor of pinholes formation is due to the presence of foreign impurities with respect to shadow effects. However, Schaer et al. suggested that any additional processes (e.g. oxidation or delamination) which will occur after the formation of pinholes are very dependent on the test conditions. The research is conducted on multi-layered OLED samples that are made up of ITO/copper-phthalocyanine (CuPc)/4,4'-bis(N-(1-naphthyl)-N-phenyl-amino)biphenyl ( $\alpha$ -NPD)/ $\text{Alq}_3$  (doped with rubrene)/ $\text{Alq}_3$  (pure)/lithium fluoride (LiF) that is covered with aluminum (Al). All the samples are tested at two different environmental conditions to investigate the effect of water vapor and oxygen presence towards the OLEDs.

For the experiment of water vapor effect at room temperature, it is found that the devices are not functioning within a few hours due to a rapid formation of dark spots. It is also observed that the dark spots develop at particular areas, as well as at the edges of Al film cathode. However, the numbers of dark spots are constant throughout the time. The authors believed that some entry ports such as pinholes must have appeared on the device's surface area which is due to the presence of small particles, but big enough to penetrate the Al film cathode during the cathode deposition process. This assumption is made by Schaer and his co-researchers because it is acknowledged that Al film acts as an excellent protective barrier from water vapor. Once pinholes are created, they will allow the penetration of water vapor into the OLEDs (Fig. 4(a)).

As proposed by the authors, electrochemical reduction of water can take place due to high electrical supply consumed and even possible in the absence of strong electrolyte, especially for low work function cathodes used in OLEDs. Eventually, this reaction will lead to hydrogen gas evolution which will induce the formation of bubbles under the cathode surface layer as illustrated in Fig. 4(b). The authors proposed that the bubbles will finally burst after they have reached a certain level of critical gas pressure since the maximum diameter of the bubbles are found only limited to 20  $\mu\text{m}$ , proved by using a Scanning Electron Microscopy (SEM) equipment. Due to the burst, the Al surface layer will be lifted rigorously and resulted in a deterioration at the interface of cathode/organic layer. Consequently, extra pinholes for penetration of water vapor will be increased with respect to the "bursting" phenomenon as shown in Fig. 4(c).

The hydrogen gas evolution which leads to the formation of bubbles under the Al layer will finally initiate the electrode delamination process. The evidence of such assumption is verified after conducting a peel-off test by using scotch tape where the adhesion of Al surface layer with the organic film becomes weaker after the degradation. As an outcome, cathode would not be able to work efficiently as the current injection into the Alq<sub>3</sub> layer is disrupted, explicating why the dark spots are developed on the OLED surfaces.

This finding is paralleled with the previous study conducted by Do et al. [50], where the authors also believed that some morphological changes on Al electrode and deformation of the organic layer underneath are due to the presence of water which is introduced from a humid atmosphere. Eventually, an electrochemical process will take place and lead to gasses evolution. In contrast with the result found by Schaer et al. as discussed previously, Do and his co-workers proposed that the morphological changes on top of Al electrode are varied with time; from tiny circle spots to growing disks with central sharp peaks about 200 nm height. Then, these disks will eventually be changed into domes and finally formed crescent shapes due to domes shrinkage (burst effect). However, Do et al. did not clarify and explain on the process of which the water molecules could enter and penetrate through the OLED samples.

On the other hand, Schaer et al. [49] have also studied the growth mechanism of dark spots under pure oxygen gas. In this particular case, the authors have conducted two distinctive experiments under both unbiased and biased conditions. For both conditions, similar results are observed where the dark spots' shape and morphological change is relatively different as compared to the previous water vapor experiment. Moreover, the dark spots evolution is found to be much slower by three orders of magnitude than the growth of dark spots in the water vapor test. Furthermore, the dark spots appeared for both conditions are associated with the presence of tiny pinholes which are confined within the cathode/organic interface of the OLEDs caused by the presence of foreign impurities. These pinholes permitted the permeation of oxygen gas into the stack of OLED layers which causes additional degradation processes to occur.

Particularly for the unbiased condition, all the samples are tested at different temperatures of 40 °C and 70 °C. It is found that the black spots growth and diameter is directly proportional to the temperature and time, respectively. In addition, the dark spots are formed in a perfect circular manner and are comprised well-defined voids for oxygen penetration, suggesting that there is no “bursting” phenomenon like in water vapor case. Furthermore, the dark spots growth is noticed to be limited by the size of pinholes gap. The authors also have interestingly discovered that at a certain time, the growth of dark spots is stopped and stay-stilled.

Schaer and his co-researchers explained that an oxide layer of 2 nm might be formed at the cathode/organic interface area due to oxidation of the Al electrode as illustrated in Fig. 5(a). The authors added that this process is possible to occur even at room temperature with less than one hour. As the oxide layer is formed, the molecular volume of the cathode will continue to increase and could be adequate enough to seal the pinhole due to aluminum oxidation as shown in Fig. 5(b). During this time, no dark spots will be formed since the oxide layer formed is still not able to fully hinder the electron injection from the Al cathode into the organic layer.

The authors also mentioned that the layer of oxide produced throughout that time is about 1.5 times larger than that consumed aluminum metal during the oxidation process. Thus, as time goes by, the increment in molecular volume will increase and gradually become too compact that could lead to an electrode delamination as depicted in Fig. 5(c), which will completely impede the electron injection into the organic layer, explaining how dark spots are possible to emerge in the emissive area.

The delamination process also will accelerate the infiltration of oxygen into the dark spots region. Ultimately, this oxygen permeation

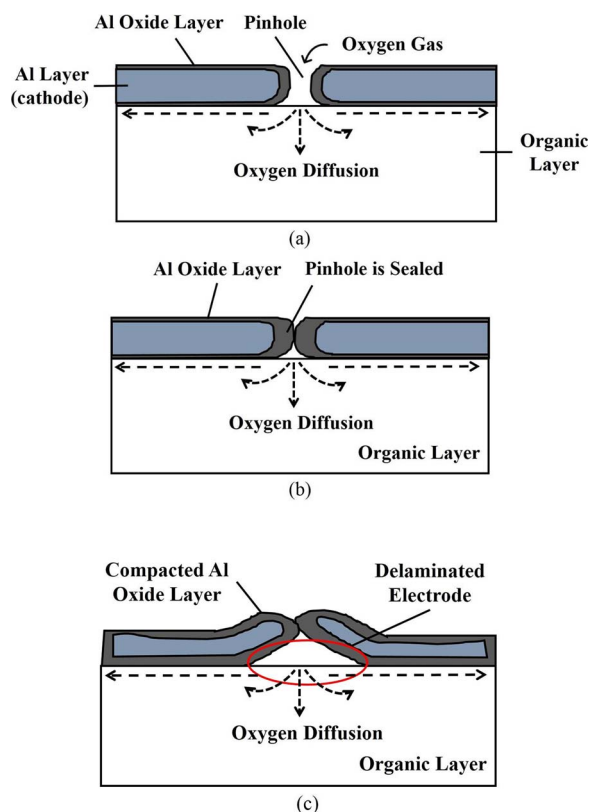


Fig. 5. Mechanism of dark spot growth: (a) oxide layer is formed due to oxygen permeation, (b) pinhole is sealed due to increment of molecular volume, and (c) delamination of electrode will block electron injection.

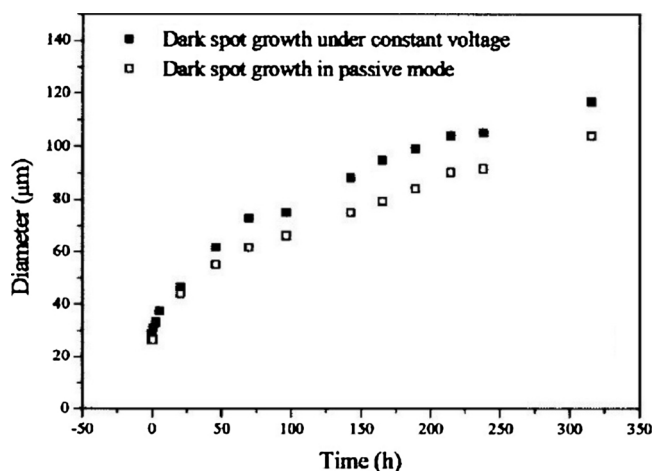


Fig. 6. Diameter of dark spots vs time in a pure oxygen gas for biased and unbiased conditions (printed with permission, Adv. Funct. Mater. 11, 116).

will cause a continuous action of oxidation at Al cathode which will give rise to the growth of the dark spots diameter (Fig. 6). In a different experiment done by Lim et al. [51], they proposed that the growth rate of dark spots is correlated linearly with the pinhole size because more water or oxygen can be penetrated into a larger pinhole.

Meanwhile, the dark spots produced in a biased condition are relatively similar with the unbiased condition, except for the formation of circle gray rings surrounded the rough core of dark spots as shown in Fig. 7. Captivatingly in biased case, the organic layer underneath the area of dark spots are stuck together with Al cathode after a peeled off test is done by using scotch tape. However, the authors justified that the circle grey rings are not the electrode material attached due to the

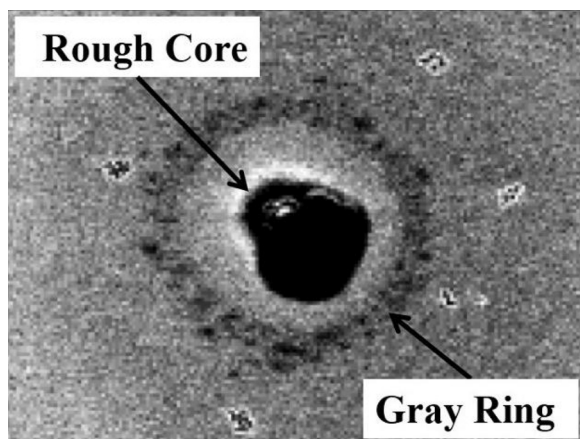


Fig. 7. Formation of circle gray rings in unbiased condition (printed with permission, Adv. Funct. Mater. 11, 116).

peeled off process. They suggested that these rings are the material of oxidized  $\text{Alq}_3$  due to an oxidation process.

Under a biased condition, Schaer and his co-researchers proposed that a photo-oxidation of organic layers (an oxidation process caused by the action of light) with respect to the formation of triplet oxygen has occurred. However, in this case, the authors stated that the photo-oxidation might take place due to excited molecular states through the recombination of injected holes and electrons during the operational of the device. This reaction will eventually cause the reorientation or recrystallization of the chemically altered molecules at the organic layers. Time by time, morphological appearances at electrode/organic interface will be deteriorated and their strong adhesion will become weaker and will give rise to dark spots formation on the OLED emitting surfaces. As a result, luminescence efficiency of the devices will be degraded. In this particular experiment, the authors never mentioned the root cause of the photo-oxidation reaction whether it is caused by the pinholes due to the presence of foreign particles or else. However, tiny pinholes can be assumed to present, since the dark spots produced are almost identical with the unbiased case, as stated by the authors before.

In summary, foreign impurities such as dusts or any other contaminated particles can be signified as one of the pivotal root cause in dark spots formation which eventually will lead to a total malfunction of an OLED device. As discussed by the literatures earlier, the foreign impurities are frequently introduced during the fabrication process and are the major reason for the formation of pinholes that are created on top of the OLED surface due to shadow effects. These pinholes will further operate as a permeation pathway for the water vapor and oxygen gas into the OLED samples. These environmental elements will trigger other damaging processes such as gasses evolution, oxidation and delamination process before dark spots are formed. Table 1 depicted the summary of the mechanisms of dark spots formation with respect to the presence of foreign impurities and pinholes.

### 3.2. High electric current intensity

Dark spots are also believed to be developed due to a high and unbalanced flow of electric current distribution. Miho et al. [52] have conducted an investigation on the nuclei structure of dark spots by utilizing three-organic-layers OLEDs of ITO/NPB/ $\text{Alq}_3$  (doped with quinacridone)/ $\text{Alq}_3$ /Al. The total thickness of the organic layers is ranging from 1000 to 1500 Å with an emitting area about  $0.2\text{ cm} \times 0.2\text{ cm}$ . The authors have discovered seven types of nuclei structures in the dark spots after operated the OLEDs for less than 10 min. They are including grain cluster (grains that formed a cluster), grain cluster and stain, protrusion, a gap in the cathode, broken cathode, pinhole and particle.

However, after completed some inspections on the nuclei by using SEM and Scanning Ion Microscopy (SIM), Miho et al. noticed that the grain cluster is the most common type of nuclei structure to appear in the dark spots. This nuclei structure is known as “Al grain cluster” since the authors found that this type of nuclei has a similar composition as in Al cathode. Additionally, Miho and his co-researchers managed to obtain the cross section of Al grain cluster nuclei by using Focused Ion Beam (FIB). From their observation, three types of cross section structures are found. They are (1) only cavity is formed between the cathode and the organic layer, (2) only foreign particles are noticed and (3) the combination of both cavity and foreign particles are observed between the cathode and the organic layer. These cross section structures are illustrated as in Fig. 8(a)–(c).

Moreover, by utilizing the Transmission Electron Microscopy (TEM), the authors also successfully did a detail investigation on the cross section structure of Al grain cluster nucleus. The result revealed that the nucleus of the Al grain cluster structure is covered with a number of small cavities, specifically in the Al cathode area. In addition, there is also a hole found that penetrated the organic layer. Based on this finding, the authors have proposed a mechanism on how such defects can appear on the OLEDs and lead to dark spots formation as shown in Fig. 9(a)–(c).

According to Miho et al., due to the concentrated electric current flows from ITO anode terminal to Al cathode terminal, some Al atoms from the cathode terminal will migrate into the organic layers through the electro-migration process (Fig. 9(a)). At the same time, some of the electric currents that flow into the cathode terminal will generate heat energy which causes the organic materials to decompose into gas and some other solid products.

The produced gas will eventually form a cavity between the ITO and organic interface as shown in Fig. 9(b). Meanwhile, the newly arrived Al atoms at the ITO anode will combine or react with the solid products and form some crystalline foreign particles. These foreign particles which are originated from Al cathode will create the Al grain cluster. This explains why the Al grain cluster comprised an identical material as in Al cathode.

These cavities and crystalline foreign particles will obliterate the structure of organic layer and form dark spots since electrons cannot be injected due to the deterioration of injection path. Finally, Al grain cluster is formed which extends from the Al cathode as elucidated in Fig. 9(c). Miho and his co-researchers also added that once the cavities are formed, only then oxygen and moisture can penetrate into the OLEDs which will further hasten the dark spots growth even when there is no electrical supply.

A year before, Cumpston and Jensen [53] have reported that the dark spots in polymer-based electroluminescent devices are also caused by the unbalanced of electric current distribution. Nevertheless, in contrast with the research conducted by Miho et al. before, Cumpston and Jensen believed that a number of defects might have already occurred within the OLED structures which could lead to a high current density event. However, the authors did not specify the process in details on how the defects can appear within the devices in the first place. The defects stipulated are including the presence of tiny holes or disparate microstructures in a region which might have a different conductivity aptitude. Moreover, Cumpston and Jensen also added that the unbalanced distribution of current density is induced by the variations in surface roughness between the interface of ITO anode and Al cathode with a polymer layer. The variations in approachability of electrons ( $e^-$ ) to conduct the electric current may result in differences of electric field intensity and current density as illustrated in Fig. 10.

This point of view is supported by Gautier et al. [54] who have investigated the nature process of an external damage on polymer/metal during the same year. They have found that the surface roughness of the polymer employed is approximately 15 Å. On the other hand, the surface roughness for the ITO and Al material that flanked the polymer is about 27 Å and 25 Å, respectively. Gautier et al. clearly stated that the

**Table 1**

Summary of the mechanisms of dark spots formation with respect to the presence of foreign impurities and pinholes.

| Author          | Materials and testing conditions for OLED samples                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Process of dark spots formation                                                                                                                                                                                        | Ref. |
|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| McElvain et al. | <ul style="list-style-type: none"> <li>ITO/TPD/Alq<sub>3</sub>/Mg/Ag</li> <li>Ambient conditions (not further specified)</li> <li>Low electrical stress</li> <li>Constant voltage of 4.5 V is applied</li> <li>Initial current density is 3–5 mA/cm<sup>2</sup></li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Foreign particles<br>↓<br>Pinholes<br>↓<br>Oxidation process<br>↓<br>Delamination process<br>↓<br>Dark spots formation                                                                                                 | [46] |
| Aziz et al.     | <ul style="list-style-type: none"> <li>ITO/NPB/Alq<sub>3</sub>/Mg/Ag</li> <li>The OLEDs are stored at room temperature in dry air and in humid air at 100% RH</li> <li>The exposure time are 2, 6 and 17 h</li> <li>The reason of pinholes formation is not been discussed</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Pinholes or Humidity (from outside)<br>or<br>Residual moisture (within the organic layer)<br>↓<br>Alq <sub>3</sub> hydration<br>↓<br>Crystallization of Alq <sub>3</sub> amorphous film<br>↓<br>Cathode delamination   | [47] |
| Lim et al.      | <ul style="list-style-type: none"> <li>ITO/PEDOT/PPV/Ca/Ag</li> <li>Ambient conditions (21 °C, 60–70% RH)</li> <li>Power source of 8.5 V is used</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Foreign Particles<br>↓<br>Pinholes<br>↓<br>Oxidation & delamination process<br>↓<br>Dark spots formation                                                                                                               | [48] |
| Schaer et al.   | <ul style="list-style-type: none"> <li>ITO/CuPc/α-NPD/Alq<sub>3</sub> (doped with rubrene)/Alq<sub>3</sub> (pure)/LiF (covered with Al)</li> <li>Threshold voltage value is 3.5 V</li> <li>Constant luminosity of 100 cd/m<sup>2</sup> (to avoid thermal stress)</li> <li>For the experiment on the effect of water vapor:</li> <li>Samples are tested at relative humidity of 75% and under applied bias</li> <li>For the experiment on the effect of pure oxygen gas:               <ul style="list-style-type: none"> <li>High-purity gasses with less than 1 ppm of residual contaminants are used (to ensure the gasses are free from water vapor)</li> <li>The gas pressure inside the box is around 1 bar</li> <li>The samples are tested under two conditions:                   <ul style="list-style-type: none"> <li>(a) Unbiased</li> <li>(b) Biased</li> </ul> </li> <li>For unbiased condition, the samples are tested are 40 °C and 70 °C for comparison purpose</li> <li>For biased condition, the test condition is not specified</li> </ul> </li> </ul> | Effect of water vapor experiment:<br>Foreign Particles<br>↓<br>Pinholes<br>↓<br>Electrochemical reaction (Reduction of water)<br>↓<br>Hydrogen gas evolution<br>↓<br>Delamination process<br>↓<br>Dark spots formation | [49] |
| Do et al.       | <ul style="list-style-type: none"> <li>ITO/TPD/Alq<sub>3</sub>/Al</li> <li>The samples are stored in 60% RH for 10 days</li> <li>Power supply of 20 V and 17 V have been used at different times (20, 25, 40 and 45 min)</li> <li>There is no further explanation about the entrance path of water like other research (e.g. pinholes).</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Water presence<br>↓<br>Electrochemical reaction (Reduction of water)<br>↓<br>Gases evolution<br>↓<br>Morphological changes<br>↓<br>Dark spots formation                                                                | [50] |

difference in the surface roughness could result in deficiency during the diode operation process.

Furthermore, according to Cumpston and Jensen, these presumed defects will cause a short circuit to take place in the electroluminescent devices and will result in an unexpected diversion of the current into the short. As an outcome, large electric current will be generated underneath the Al cathode layer and localized heating around the short circuit will be produced. Al metal atoms will be carried along by the momentum of electrons that dashed into the short circuit in a circular manner and accumulated Al metal atoms will be created at the center of the defect. Eventually, this action will result in a circular boundary as shown in Fig. 11. Finally, the Al cathode at the circular boundary will become thin enough which no longer able to inject electrons to cross the boundary limit. As soon as electrons are unable to pass through the incapacitated cathode layer (at the center region), non-emissive dark spots will be formed within the devices.

In 2007, Gardonio and his co-researchers [55] have reported the degradation created in multi-layered structures of OLED samples (ITO/α-NPB/Alq<sub>3</sub>/Alq<sub>3</sub>/Al) that are fabricated, kept and operated under

ultra-high vacuum (UHV) in between 10<sup>−7</sup> to 10<sup>−9</sup> mbar. Thus, the degradation event associated with humidity and water penetration can be eliminated. The samples are operated after 30 min of the fabrication process with a threshold voltage of 30 V. Meanwhile, the chemical composition and morphology change of the OLED cathode is examined and assessed by using scanning X-ray Photoelectron Spectromicroscopy (μ-XPS).

Gardonio et al. believed that the failure and degradation of the OLED samples are caused by the presence of local short circuits due to ‘irrepressible’ imperfections in the OLED structures such as topographical defects, morphological contours and surface roughness. The authors said that these local electrical shorts will cause an intensification of local temperature and lead to heat generation. Eventually, local decomposition processes will occur between the ITO and organic structures interface due to an upsurge in heat as a high voltage is employed during the OLED operation (≈30 V).

As a result, volatile products that consist of indium (In) and carbon (C) will be emancipated within the layers. In addition, the ITO's major element which is indium oxide (In<sub>2</sub>O<sub>3</sub>) also will be reduced and

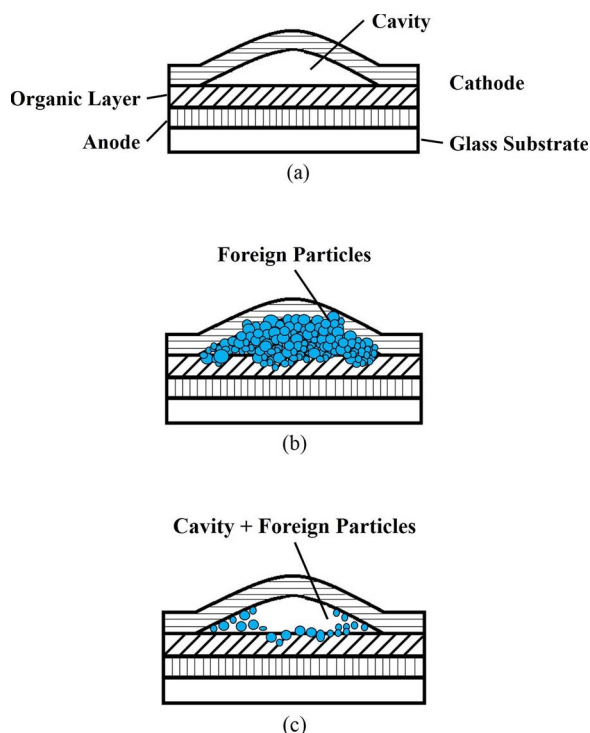


Fig. 8. Cross section of Al grain cluster nuclei: (a) only cavity is formed, (b) only foreign particles are present, and (c) both cavity and foreign particles are observed.

released oxygen (O) as well as  $\text{InO}_x$  species during the decomposition actions. The released of these volatile products will initiate an oxidative process and lead to a local delamination of cathode, since the volatile products are intermingled between the Al and organic interface. They have discovered that the concentration of Sn in the ITO anode is reduced about 8 to 10 times as compared to non-operation anode.

Additionally, according to Gardonio et al., the degradation of OLED samples operated in a vacuum condition show no noticeable deformations of the cathode. However, obvious cathode deformations can be observed when the devices are operated in an air-exposed environment. The authors added that an identical failure mechanism is also pertinent and applicable for the OLEDs exposed to air. However, unlike deformations in a vacuum condition, the cathode of an air-exposed OLED portrays a visible volcanic-like shape as been proved in their previous study [56]. This is because the presence of oxygen and adulterated moisture is further accelerated the oxidation rate at the Al/organic interlayer. As an outcome, a locally swelled cathode or known as bubble formation will be formed and be burst due to gas overpressures. Consequently, the Al cathode will be locally disrupted, and dark spots will be emerged due to disconnected of electron injection path.

Do et al. [57] have also found morphological defects on the OLED devices after operated under a high voltage flow. When 30 V is applied on the ITO/TPD/ $\text{Alq}_3$ /Al samples, an increment of temperature about 78 °C is detected. By utilizing infrared thermal imaging radiometer, the obtained thermal image revealed that the temperature is distributed in a circular shape where the middle part encompasses a higher temperature as compared to the vicinity's temperature of the outer part. Additionally, it is also found that the middle part of the circular shape is crossed perpendicularly with an intersection at the center between ITO anode and Al cathode.

Four years later, Zhou et al. [58] have demonstrated infrared images of a disproportionate feature of temperature intensity on ITO/TPD/ $\text{Alq}_3$ /Al OLEDs when the devices are operated at the voltage of 28 V or higher. However, when a lower voltage supply is employed, a contradicted outcome is reported as the temperature images featured a consistent and uniform intensity of temperature. Paralleled with the study

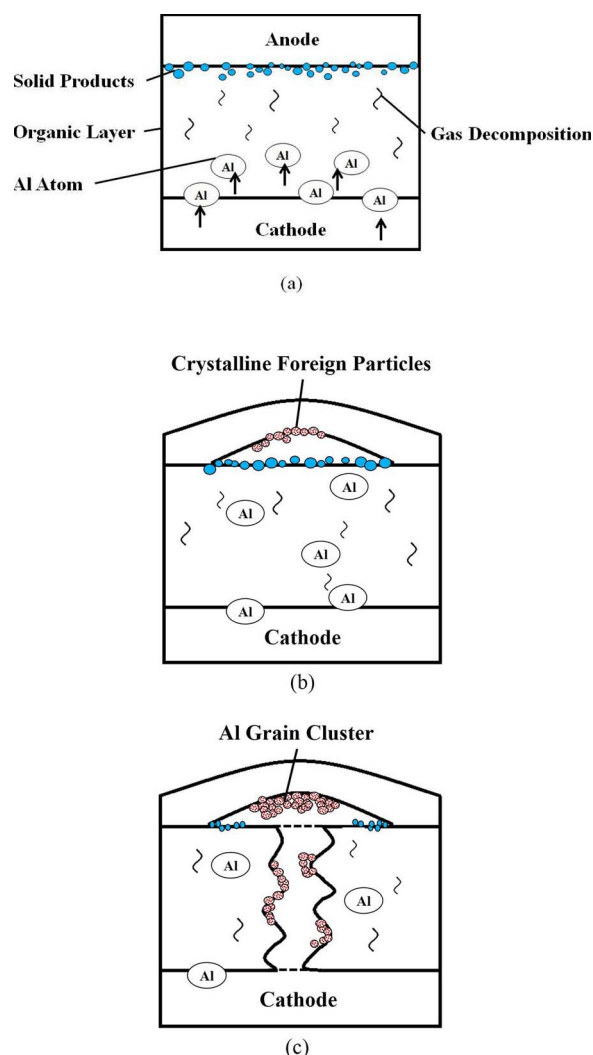


Fig. 9. Dark spot mechanism growth: (a) electro-migration process and decomposition of organic layer due to concentrated electric current and heat generation, respectively, (b) cavity is formed and crystalline foreign particles are produced, and (c) Al grain cluster is formed and protrudes from cathode layer.

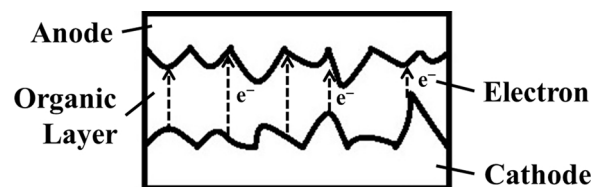


Fig. 10. Variability in surface roughness between anode, cathode and organic layer results in unbalanced of electric current distribution due to discrepancy of the electrons reachability within the OLED layers.

done by Do et al. [57], Zhou and co-workers have also found that the temperature intensity at the center of the OLEDs is the highest in which the short circuit is present. The temperature of the surrounding surface is about 86 °C and the temperature within the devices could be greater. Conversely, the authors also said that an OLED device will still be illuminated even after the electrical short circuit has appeared during the operation periods. In addition, the origin spot of the electrical short in an OLED is so intricate to verify. Hence, Zhou et al. stated that this particular issue will be a critical challenge for related-OLED researchers to overcome.

Based on the previous observations, Zhou and his co-researchers have described a detailed mechanism of degradation process with

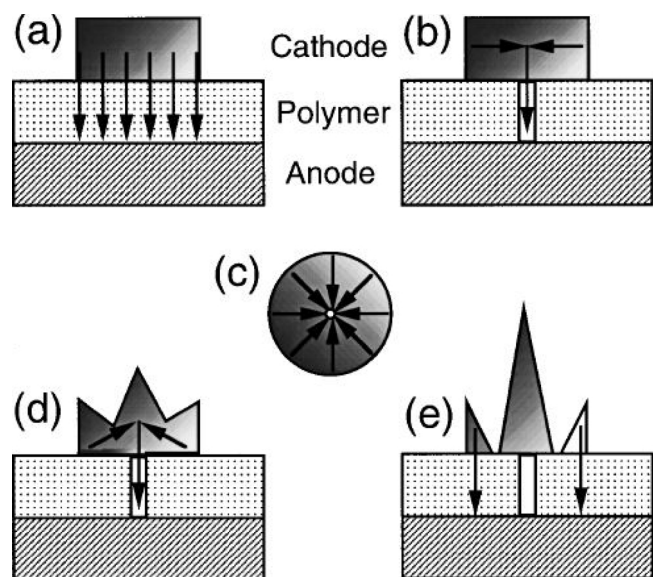


**Fig. 11.** Formation of Dark Spots: (a) normal operation, (b) diversion of current flow into short circuit, (c) large electric current dashed into the short circuit in a circular manner, (d) accumulated Al metal atoms will be created at the center of the defect, and (e) Al cathode at the circular boundary will become thin enough and not able to inject electrons to cross the boundary limit (printed with permission, Appl. Phys. Lett. 69, 3941).

regards to the formation of an electrical short circuit. When a high electric voltage is applied (above 28 V), oxygen gas and indium atoms are released due to decomposition of ITO anode. The decomposition process is likely to occur at the sites where the surface roughness greatly varies with non-uniform asperities.

Then, an electro-migration process will occur with respect to the high electric current that flows out from the positive terminal of the power source in which the indium atoms will be able to penetrate across the Alq<sub>3</sub> and TPD layer towards the Al cathode. Eventually, a number of microscopic conduction holes infiltrated through the organic layers are formed. As an outcome, electrical short circuits are induced. A short circuit endures a very huge amount of inflows current as the impedance of the short circuit is very low. Additionally, the current flows also resulted in Joule heating action which further causes the temperature in and around the short circuit to rise vigorously. The higher temperature will stimulate the crystallization of the TPD layer, as well as further hasten the decomposition of ITO and speed up the electro-migration process of the indium atoms to the anode surface. Finally, a thermal breakdown of an OLED will happen as the top of the Al film is expected to be burst into a star-shaped opening as shown in Fig. 12.

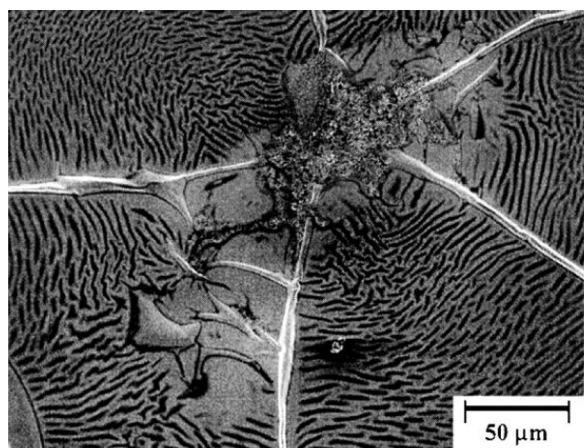


**Fig. 12.** SEM image of star-shaped opening at the top of Al film (printed with permission, Adv. Mater. 12, 265).

If a device is operated under high-temperature conditions, its thermal stability must be taken into account as it is directly related to the durability of the device. Thermal stability can merely be defined as the stability of a body to resist a molecular breakdown or micro-structural rearrangement at elevated temperatures even in oxygen-free environments [59]. Concisely, a molecule with a great stability has better resistance to decomposition action at high temperatures. Thermal stability of an OLED is innately ascertained by the degree of glass transition temperature ( $T_g$ ) of organic structures [58].

As reported by Do et al. before [57], the temperature of 78 °C yielded during the operation of devices is essentially surpassed the  $T_g$  of TPD which is around 60 °C [60,61], but lower than the  $T_g$  of Alq<sub>3</sub>. The durability and performance of OLED panels are predominantly restricted by the thermal stability of the TPD layer because that particular HTL material has a rather low  $T_g$  point [62,63]. With respect to this phenomenon, a changing on the devices appearance can perceptibly be detected as an undulated surface which is initiated by the changes between the TPD and Alq<sub>3</sub> film due to the thermal instability during the applying of high voltage flow.

Moreover, according to Do and co-researchers [57], the increase in temperature will augment the inter-diffusion process within the TPD and Alq<sub>3</sub> layers which will further influence the morphology of the samples. The inter-diffusion process is verified by observing the changes in the PL spectra as their intensities are fluctuating due to the occurrence of energy transfer from TPD to Alq<sub>3</sub> layer in the devices. Furthermore, Do et al. also believed that the thermal instability or increase in heat within the OLED samples is correlated with the roughness of the organic layer. Thus, a test on bilayer films (mixed TPD-Alq<sub>3</sub>/pure Alq<sub>3</sub>) is carried out in order to clarify this crucial matter. By using Atomic Force Microscope (AFM), the result exposed that the roughness of the bilayer films is reduced as the Alq<sub>3</sub> content in the mixed TPD-Alq<sub>3</sub> film is increased. The authors proposed that a better thermal stability can be achieved if the roughness between the organic layers is more uniform. They also suggested the usage of TPD-Alq<sub>3</sub> mixed film as a HTL in OLED devices for a better thermal stability performance.

The performance of the TPD/Alq<sub>3</sub> layers is highly influenced by the deposition rate employed during the devices fabrication as well. According to Mu et al. [64], the selection of deposition rate is very crucial because it has a great impact on the surface morphology of the organic films. By observing the SEM and AFM images of the TPD/Alq<sub>3</sub> layers, the presence of tiny pinholes ranging from 10 to 30 nm sputtered on the samples surface is reported when a high deposition rate of 0.15 nm/s is employed. Captivatingly, no pinholes are detected when 0.5 nm/s deposition rate is utilized during the double layer fabrication process. Additionally, the characterization results also illustrated a dense and smooth surface of the TPD/Alq<sub>3</sub> layers with more uniform and ordered surface roughness as compared to the low deposition rate.

In the recent decades, many researchers have been studying and developing novel, durable materials which comprised higher  $T_g$  for OLED applications, because local molecular motion that induces the crystallization process is initiated at near the  $T_g$  point. Tokito et al. [65] have revealed that a novel HTL material, triphenylamine tetramer (TPTE) embraced a high  $T_g$  of 130 °C by differential scanning calorimetry (DSC) which performed effectively better than TPD layer at high temperatures. Besides, the morphology of OLED samples which consist of TPTE film is found to be uniform and consistent even after the samples are heated for 1 h at 100 °C.

Two years later, Tokito and co-researchers [66] have synthesized several linear linkages of triphenylamine oligomers for HTL including triphenylamine trimer (TPTR), triphenylamine pentamer (TPPE), triphenylamine starburst-tetramer (TPTE(S)), as well as TPTE and TPD layer. The authors have found that the drastic drop value or critical temperature for all the triphenylamine oligomers are directly proportional to the  $T_g$  readings as shown in Fig. 13.

Moreover, the results also showed that TPD layer has the lowest  $T_g$  which is only 60 °C, followed by TPTR, TPTE(S) and TPTE where the  $T_g$

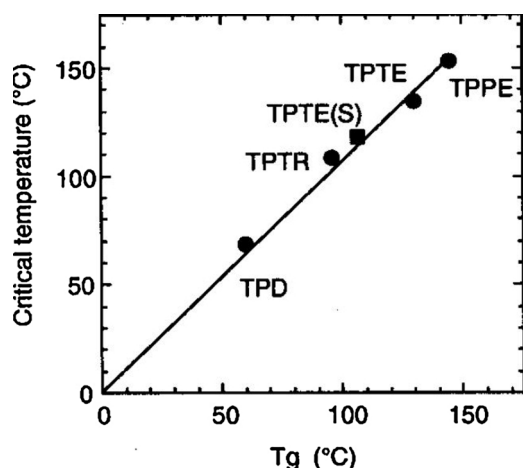


Fig. 13. Linear relationship between critical temperature (°C) and  $T_g$  (°C) (printed with permission, Macromol. Symp. 125, 181).

is equal to 110 °C, 125 °C and 135 °C, respectively. Meanwhile, TPPE has the highest thermal stability in which the  $T_g$  is about 155 °C. Nevertheless, the quantum efficiency of the TPPE layer (0.59%) is the lowest as compared to another triphenylamine layers (1%). Tokito et al. posited that some impurities or contaminations might have occurred during the deposition process. The key reason, however, is still not clearly comprehended.

The results found by Tokito et al. [65,66] are found to be relatively similar to data obtained by Fujikawa et al. [67] who have conducted a study on the same HTL materials. In addition, Fujikawa and co-researchers have compared the half-decay lifetime performance of three different types of HTL materials which are TPD,  $\alpha$ -NPB and TPTE at constant current supply about 100 mA/cm<sup>2</sup> with an initial luminance of 3100 cd/m<sup>2</sup>. The luminance intensity will be recorded when 50% of the initial luminance value has decreased. The  $T_g$  for TPD,  $\alpha$ -NPB and TPTE is around 60 °C, 95 °C and 135 °C, respectively. The results indicated that the material with lower  $T_g$  tends to degrade faster. As illustrated in Fig. 14, the lifetime of a TPD device is the shortest which is only 5 h until it reduced to 50% of the luminance intensity, whereas  $\alpha$ -NPB managed to withstand about 8 h and TPTE samples are remarkably able to sustain approximately for 22 h.

Furthermore, Fujikawa et al. have compared the lifetime of TPTE and TPD layers deposited on OLED samples operated at continuous operation. The samples are tested with an initial luminance of 300 cd/m<sup>2</sup> at different temperatures (room temperature, 85 °C, 105 °C and

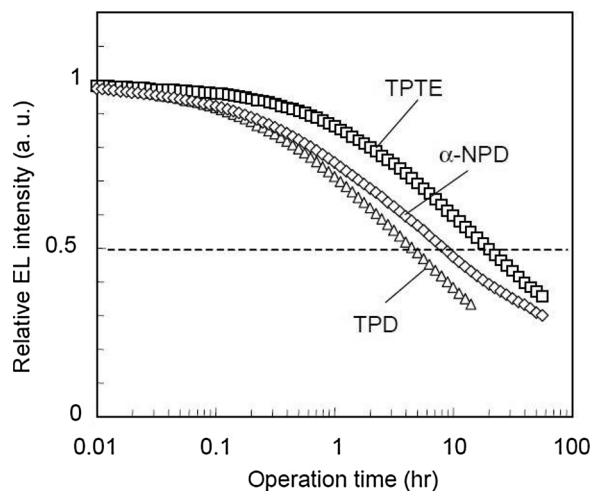


Fig. 14. Half-decay lifetime performance HTL materials (printed with permission, Materials Research Society Symposium Proceedings. 621, Q3).

120 °C). The authors stated that TPTE layers managed to survive for 15000 h at room temperature, 1700 h at 85 °C, 680 h at 105 °C and 270 h at 120 °C. In contrast, an extremely short lifetime is recorded for the TPD deposited layer as the samples are failed after operated for less than 1 min at 85 °C. On top of that, the linear linkage of triphenylamine oligomers have also encompassed the ability to produce uniform films on the glass substrates and offer a better thermal stability, especially TPTE film when operated at high temperatures.

In summary, the concentrated current flows and the unbalanced of electric current distribution can generate an excessive heat due to a high local temperature. Time by time, the heat produced will initiate the decomposition of organic materials in the OLED layers and produced volatile products. In some cases, electro-migration can be happened as well, due to a high electric current that flows from anode to cathode or into short circuits. The short circuits are mainly created due to the presence of foreign particles on the OLED surface or caused by the varieties of surface roughness between the OLED's layers which will result in the wavering of electric field intensity. Moreover, the  $T_g$  of the materials chosen in fabricating the OLED structures is a vital factor too, since the durability and performance of OLED devices is predominantly restricted by the thermal stability. In brief, Table 2 exemplified the summary of mechanisms of dark spots formation with respect to the high electric current intensity.

#### 4. Prevention steps to reduce dark spots formation

##### 4.1. Fabrication process and materials selection

The growth of dark spots can be caused by several factors as suggested earlier by the past researchers and are well-noticed to be very unpredictable. It is also known, the formation of dark spots will degrade the luminance performance of an OLED device. Frequently reported, the preferable conditions which can finally lead to dark spots formation are included exposure to contaminated surroundings and different environment temperatures, as well as exposure to water vapor or humid air. Concerned with this problematic issue, a number of prevention steps to minimize the dark spots formation have been proposed.

Lim et al. [48] have suggested a few precaution steps that need to be taken which are quite similar as recommended by McElvain et al. [46]. The authors have recommended that the substrates and the anode surfaces must be carefully cleaned so that they are free from specks of dusts or particles. In this way, the presence of pinholes due to the particles' shadow effects can be eliminated. Moreover, polymer solution during OLED's fabrication process should be filtered in a controlled and cleaned environment. In addition, any sputtering of organic materials during the organic deposition process needs to be avoided in order to reduce the dark spots formation and to prolong the lifespan of an OLED device.

Furthermore, materials selection for OLED structures also plays a significant role in order to prevent the growth of dark spots. According to Schaer et al. [49], chemical substances used for adhesion between cathode/organic interface and cathode with low work function materials would influence the rate of water diffusion and enhance the water reduction process, respectively. Moreover, the authors also proposed that Al acts as an excellent cathode material due to its external protective oxide layer, as well as recommended to avert the usage of poly (phenylene vinylene) polymers as an organic layer in OLED structure since these polymers are very susceptible to oxidation process about 10 times faster than Alq<sub>3</sub>. Besides, there are other materials that would oxidize more quickly and aggressively with the presence of oxygen such as alkali metals and alkali earth metals.

To date, however, the encapsulated OLEDs constructed on the basis of poly (phenylene vinylene) copolymer, known under the trade name of "Super Yellow" (SY) are shown stable performances. The OLEDs made up of the SY is reported to have a luminous efficacy greater than 15 lm/W [68], exhibit a very low turn-on voltage of 2.6 V (measured at

**Table 2**

Summary of the mechanisms of dark spots formation with respect to the high electric current intensity.

| Author              | Materials and Testing Conditions For OLED Samples                                                                                                                                                                                                                                                                                                                                                                                                                          | Process of Dark Spots Formation                                                                                                                                                                                                                                                                                         | Ref. |
|---------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Miho et al.         | <ul style="list-style-type: none"> <li>ITO/NPB/Alq<sub>3</sub> (Qd doped)/Alq<sub>3</sub>/Al</li> <li>OLED samples are operated for less than 10 min (most cases less than 2 to 3 min)</li> <li>5 V of voltage is applied with current density of 5 mA/cm<sup>-2</sup></li> </ul>                                                                                                                                                                                          | Concentrated electric current flows (From ITO anode to Al cathode)<br>↓<br>Electro-migration process<br>↓<br>Heat is generated<br>↓<br>Decomposition of organic materials<br>↓<br>Cavity is formed<br>↓<br>Crystalline foreign particles are produced<br>↓<br>Formation of dark spots                                   | [52] |
| Cumpston and Jensen | <ul style="list-style-type: none"> <li>ITO/MEH-PPV/Al</li> <li>A constant voltage is used</li> <li>Dark spots are occurred approximately at current density of 100 mA/cm<sup>2</sup></li> </ul>                                                                                                                                                                                                                                                                            | Surface defects/varieties in surface roughness<br>↓<br>Variations in electron approachability<br>↓<br>Short circuit is formed<br>↓<br>Unbalanced of electric current flow & heat produced<br>↓<br>Formation of dark spots                                                                                               | [53] |
| Gardonio et al.     | <ul style="list-style-type: none"> <li>ITO/α-NPB/Alq<sub>3</sub>/Alq<sub>3</sub>/Al</li> <li>Threshold voltage of 30 V is applied</li> <li>OLED samples are operated in ultra-high vacuum (UHV) condition</li> </ul>                                                                                                                                                                                                                                                       | Local short circuit<br>↓<br>Heat generation<br>↓<br>Decomposition process<br>↓<br>Volatile products are produced<br>↓<br>Oxidative processes are initiated<br>↓<br>Local delamination of cathode<br>↓<br>Formation of dark spots                                                                                        | [55] |
| Zhou et al.         | <ul style="list-style-type: none"> <li>ITO/TPD/Alq<sub>3</sub>/Al</li> <li>The OLED samples are tested at both low and high voltage stress</li> <li>Images of OLED surface temperature are recorded at:               <ul style="list-style-type: none"> <li>- 18 V ≈ 35 °C</li> <li>- 20 V ≈ 37 °C</li> <li>- 22 V ≈ 40 °C</li> <li>- 24 V ≈ 43 °C</li> <li>- 26 V ≈ 46 °C</li> <li>- 28 V ≈ 49 °C</li> <li>- 30 V ≈ 55 °C</li> <li>- 33 V ≈ 86 °C</li> </ul> </li> </ul> | Electrical shorts<br>↓<br>Decomposition of anode (Especially at the site of non-uniform surface roughness)<br>↓<br>Electro-migration process<br>↓<br>Microscopic conduction holes are created<br>↓<br>Heat generation<br>↓<br>Crystallizations of TPD layer<br>↓<br>Bursting of Al film<br>↓<br>Formation of dark spots | [58] |

1 cd/m<sup>2</sup>) [69] with higher luminance (69330 cd/m<sup>2</sup>) as compared to poly (9, 9-dioctylfluorene) layer (3371 cd/m<sup>2</sup>) [70]. In common practice, SY is widely used as an emissive layer [71–77] or as an active film [78] in an OLED structure. Hence, choosing particular and appropriate

**Table 3**

Organic layer/s used for OLED device structures [79].

| Type of Organic Layer/s | OLED Device Structures                                              |                 |         |
|-------------------------|---------------------------------------------------------------------|-----------------|---------|
|                         | Organic Stack                                                       | Anode/Substrate | Cathode |
| Single Layer            | Alq <sub>3</sub><br>NPB                                             | ITO or Glass    | Ca/Ag   |
| Double Layers           | Alq <sub>3</sub> /NPB<br>NPB/Alq <sub>3</sub>                       |                 |         |
| Triple Layers           | Alq <sub>3</sub> /NPB/Alq <sub>3</sub><br>NPB/Alq <sub>3</sub> /NPB |                 |         |

materials for combinations of OLED structures is vital since any deterioration processes that could lead to dark spots formation can be eliminated or at least be minimized.

With regards on combinations of OLED structures, Liew et al. [79] have conducted a study which aimed to investigate the effect of a combination of organic layers on dark spots growth. Three types of organic layer are fabricated for this particular study as shown in Table 3. Two type of substrates are used in this study; ITO and glass substrates. The cathode utilized for all devices are the same which is a combination layer of Ca/Ag. The thickness of NPB, Alq<sub>3</sub>, Ca and Ag are 600, 600, 100 and 1500 Å, respectively. All the OLEDs are fabricated and stored in an ambient surrounding of 23 °C and 75% RH for a certain period with no electrical influences or external stimulus.

In order to achieve the objective of this study, a set of experiments has been carried out. For the first experiment, the authors intended to study the effect of different thickness of the organic layer. In this case, the single layer of organic stack of ITO/Alq<sub>3</sub>/Ca/Ag has been utilized. The result revealed that the growth of dark spots in the non-operated devices is notably independent on the thickness of Alq<sub>3</sub> which is ranging from 50 to 6000 Å.

Next, both ITO and glass substrates are deposited with layers of organic stack in order to investigate the influence of different substrates on the dark spots formation. For single layer devices, the rate of dark spots growth spotted is about 1.3 μm<sup>2</sup>/min and 6.0 μm<sup>2</sup>/min in glass/NPB/Ca/Ag and ITO/NPB/Ca/Ag, respectively. Thus, glass substrate showed a better performance since the growth rate of dark spots is much slower as compared with the growth rate in ITO substrate. Besides, Liew et al. have also discovered that the dark spots growth rate that used NPB as the first organic layer is much faster as compared to Alq<sub>3</sub> experiment as shown in Fig. 15. The first organic layer of single layer devices which is glass/NPB/Ca/Ag and ITO/NPB/Ca/Ag is replaced with glass/Alq<sub>3</sub>/Ca/Ag and ITO/Alq<sub>3</sub>/Ca/Ag, respectively. As illustrated in Fig. 16, it is well-noticed that the dark spots growth rate of Alq<sub>3</sub> on both ITO and glass substrates are almost similar which is about 0.6 μm<sup>2</sup>/min.

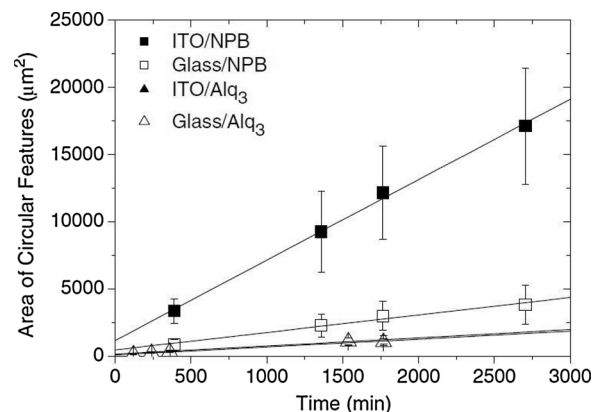


Fig. 15. Growth rate of circular features (dark spots) vs time for different type of substrates (printed with permission, Chem. Phys. Lett. 394, 275).

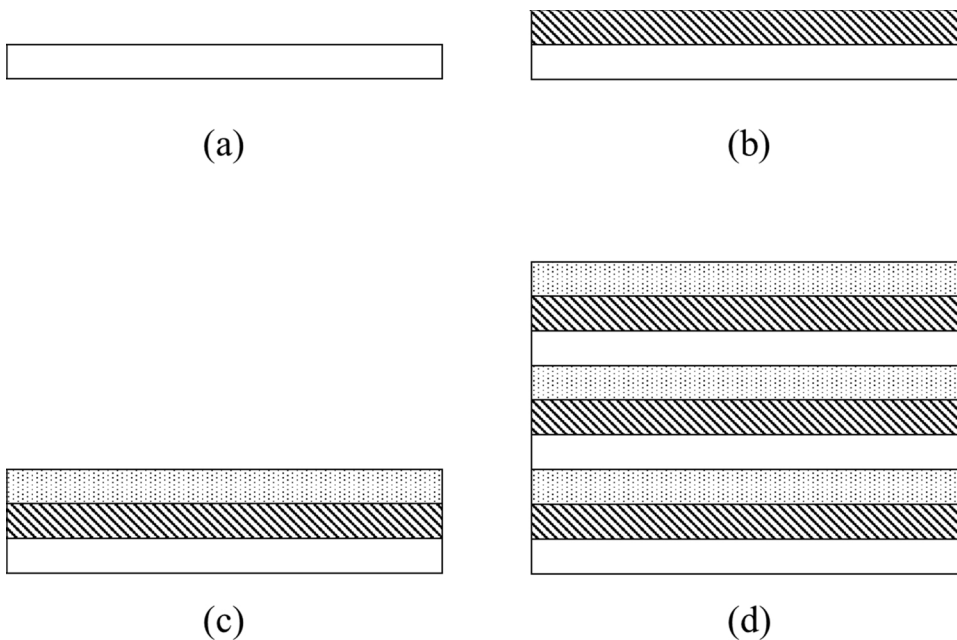


**Fig. 16.** Structure of OLED encapsulation: (a) single layer of  $\text{Al}_2\text{O}_3$ , (b) combination of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  layers, (c) hybrid layer of  $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{alucone}$  layers, and (d) three pairs  $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{alucone}$  layers..

From the graph as illustrated in Fig. 15 above, two primary subjects have been signified by the authors. First, they have found that the dark spots formation is dependent on the substrate materials. This occurrence can clearly be seen by comparing the outcome of rate of dark spots growth between ITO/NPB and glass/NPB. The second discovery is verified that the growth of dark spots dependent on the contact between the first organic layer and the substrate used. As can be seen lucidly in Fig. 15, dark spots grow faster in ITO/NPB as compared to ITO/ $\text{Alq}_3$ . This condition is further approved by implementing double and triple layers of organic stacks on ITO substrate. Significantly, the results exposed that the devices which utilized  $\text{Alq}_3$  as their first organic layer have slower dark spots growth rate than the devices that employed NPB under the same layer structure. The summarized of this particular experiment is illustrated in Table 4.

From the data gathered, Liew et al. have demonstrated that ITO/ $\text{Alq}_3$  interface featured an advantage over ITO/NPB interface. Results obtained also indicated the direct involvement of ITO/organic interface on the dark spots growth in OLED devices. Last but not least, in another experiment, the authors are able to clarify that the presence of  $\text{Alq}_3$  as an interlayer between ITO and organic stack for a nanometer thick will generate a better electron-hole current stability and contribute to an effective device performance.

As described earlier, selection for substrate materials can greatly affect the performance of an OLED. Weaver et al. [80] have specifically compared the rate of decaying luminance between plastic-based and glass-based substrates. The results showed that the luminance of the devices made on plastic-based and glass-based substrates decays to 50% and 11% of its initial luminance in 3800 h, respectively. Conversely, devices of glass-based substrates take around 10700 h to degrade into

50% of its initial luminance.

The effect of materials selection for OLED structure also has been done by Han et al. [81]. They have manipulated the contents of  $\text{Alq}_3$ , TPD and a mixture of both substances which varies from 2, 10, 50 and 90% of the volumetric ratios. Before the organic thin films are deposited on ITO-coated glass substrates or slide glass plates. The ITO-coated glass substrates surface is cleaned by using detergent, clean water, acetone and ethanol in an ultrasonic cleaner. Meanwhile, the slide glass plates are cleaned for 30 min at 90 °C with piranha solution ( $\text{H}_2\text{O}_2$ :  $\text{H}_2\text{SO}_4$  = 30:70 v/v) and followed by cleansed with water, ethanol and acetone. However, they have found that a crystallization process still occurs in the interfacial region of  $\text{Alq}_3$ /TPD layer even cleanliness precaution steps are taken beforehand.

In general, as observed from prior studies, it can be concluded that the right material selection for an OLED structure is the best solution to eliminate or reduce the formation of dark spots in the devices even when the experiments are conducted in a controlled environment.

#### 4.1.1. Passivation techniques

Subsequently, researchers worldwide also have taken an initiative and developed an approach called passivation technique in order to minimize the effects of moisture and humidity infiltration on the OLED layers. Desiccator and encapsulation techniques are the two main approaches that are frequently will be utilized by the OLED researchers and manufacturers [82].

Desiccator technique can be defined as the method of applying desiccants or drying agents such as calcium oxide or silica gel into a device. In OLED cases, desiccants are only required to be implemented on the interior wall of the devices. Virtually, this technique has less market value since it requires very wide walls where the dimensions of OLED devices must be compromised. Vacuum vapor deposition, spin coating and sputtering the desiccants between the top seals and the substrate of an OLED are the common examples of methods in which a desiccant layer can be implemented over the organic layer of an OLED.

As compared to desiccator technique, encapsulation method is proven to be the most effective approach in order to prevent the access of moistures into the OLED device. Yamashita et al. [83] have established that the lifetime of encapsulated OLED is almost four times longer as compared to non-encapsulated OLED which is only about 2.5 h when operated in an opened-air environment. In their experiment, poly-*p*-xylylene (PPX) and poly-2-chloro-*p*-xylylene (PCPX) are

**Table 4**  
Organic layer/s used for OLED device structures [79].

| Device Structure |                                        |         | Growth Rate of Dark Spots ( $\mu\text{m}^2/\text{min}$ ) |
|------------------|----------------------------------------|---------|----------------------------------------------------------|
| Anode            | Organic Stack                          | Cathode |                                                          |
| ITO              | $\text{Alq}_3$                         | Ca/Ag   | ~ 0.6                                                    |
|                  | $\text{Alq}_3/\text{NPB}$              |         | ~ 0.6                                                    |
|                  | $\text{Alq}_3/\text{NPB}/\text{Alq}_3$ |         | ~ 0.6                                                    |
|                  | $\text{NPB}/\text{Alq}_3$              |         | ~ 6.0                                                    |
|                  | $\text{NPB}/\text{Alq}_3$              |         | ~ 6.0                                                    |
|                  | $\text{NPB}/\text{Alq}_3/\text{NPB}$   |         | ~ 6.0                                                    |

**Table 5**  
Summary of the encapsulation film effects on the formation of dark spots and OLED performances [92–98].

| Encapsulation material/s                                                                        | Encapsulation thickness (μm)                                          | Encapsulation technique/s                                                                      | Testing conditions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Results                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Ref. |
|-------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Silicon nitride (SiN <sub>x</sub> )                                                             | 1                                                                     | Surface-wave-plasma enhanced chemical vapor deposition (SWP-CVD)                               | <ul style="list-style-type: none"> <li>• The OLEDs are tested at 60 °C, 90% RH.</li> <li>• The authors have developed 3 different layers to be used as intermediate film in OLEDs and covered with SiN<sub>x</sub> as the encapsulation layer. The intermediate films are:               <ul style="list-style-type: none"> <li>- Inorganic silicon oxynitride (SiON) film (3 μm),</li> <li>- Organic Paralyne film (3 μm), and</li> <li>- Combination of the inorganic and organic (SiO<sub>x</sub>C<sub>y</sub>) film (3 μm).</li> </ul> </li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | <ul style="list-style-type: none"> <li>• Without any intermediate film, the formation of dark spots is detected on the OLEDs' surface after 21 h operated.</li> <li>• With the presence of inorganic SiON and organic Paralyne film, the dark spots are formed after 24 and 17 h operated, respectively.</li> <li>• Meanwhile, no growth of dark spots up to 360 h with the presence of hybrid SiO<sub>x</sub>C<sub>y</sub> in the OLEDs.</li> </ul>                                                                                                                                                                                                           | [92] |
| Al <sub>2</sub> O <sub>3</sub>                                                                  | 0.1                                                                   | ALD                                                                                            | <ul style="list-style-type: none"> <li>• The OLEDs are tested at 38 °C, 90% RH.</li> <li>• Thin film of poly (3,4-ethylenedioxythiophene) mixed with poly (styrene sulfonate) or established as PEDOT:PSS is used as the HTL.</li> <li>• The temperature and the RH are specified particularly to test the degradation of encapsulated OLEDs. The authors have also utilized different testing conditions for another aims.</li> <li>• 5 types of encapsulation layers are made, including: Luminance is tested with voltage supply of 8 V               <ul style="list-style-type: none"> <li>- None,</li> <li>- Only substrate of polyethylene terephthalate (PET),</li> <li>- Al<sub>2</sub>O<sub>3</sub>/PET,</li> <li>- Parylene/Al<sub>2</sub>O<sub>3</sub>/PET (1-pair), and</li> <li>- Parylene/Al<sub>2</sub>O<sub>3</sub>/Parylene/Al<sub>2</sub>O<sub>3</sub>/PET (2-pair).</li> </ul> </li> <li>• The OLEDs are tested at 25 °C, 45% RH.</li> <li>• The authors have deposited 25 μm of polydimethylsiloxane (PDMS) layer on top of the graphene-based film (using PET as substrate).</li> <li>• 5 different structures of OLED with distinct number of graphene layers are made, including:               <ul style="list-style-type: none"> <li>- Only PET (no encapsulation film),</li> <li>- PET/PDMS,</li> <li>- PET/2-layered graphene/PDMS,</li> <li>- PET/4-layered graphene/PDMS, and</li> <li>- PET/6-layered graphene/PDMS.</li> </ul> </li> </ul> | <ul style="list-style-type: none"> <li>• Dark spots growth are detected after 19 h with the presence of PEDOT:PSS layer.</li> <li>• No dark spots are detected within the first 50 h without the presence of PEDOT:PSS layer.</li> <li>• In both conditions, dark spots are still occurred even at different time and highly depend on the material's layer utilized.</li> <li>• The lowest WVTR value is recorded by 2-pair layers of OLEDs 2.77 g/m<sup>2</sup>/day as compared to other type of encapsulation layers.</li> <li>• However, all the OLEDs are found with a lot of dark spots, but least occurrence at 2-pair encapsulation layers.</li> </ul> | [93] |
| 1) Al <sub>2</sub> O <sub>3</sub><br>2) Parylene                                                | 1) Not stated for Al <sub>2</sub> O <sub>3</sub><br>2) Parylene = 0.1 | 1) ALD for Al <sub>2</sub> O <sub>3</sub> deposition<br>2) CVD for Parylene deposition         | <ul style="list-style-type: none"> <li>• The authors have deposited 25 μm of polydimethylsiloxane (PDMS) layer on top of the graphene-based film (using PET as substrate).</li> <li>• 5 different structures of OLED with distinct number of graphene layers are made, including:               <ul style="list-style-type: none"> <li>- Only PET (no encapsulation film),</li> <li>- PET/PDMS,</li> <li>- PET/2-layered graphene/PDMS,</li> <li>- PET/4-layered graphene/PDMS, and</li> <li>- PET/6-layered graphene/PDMS.</li> </ul> </li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <ul style="list-style-type: none"> <li>• It is found that the OLEDs lifetime is increase linearly with the number of stacked graphene.</li> <li>• However, water vapor is still able to penetrate into the OLEDs even at a slight rate. In other words, the encapsulation film is only managed to hold back the water vapor infusion at a limited time only.</li> </ul>                                                                                                                                                                                                                                                                                        | [94] |
| Graphene                                                                                        | (not stated)                                                          | CVD                                                                                            | <ul style="list-style-type: none"> <li>• The authors have deposited 25 μm of polydimethylsiloxane (PDMS) layer on top of the graphene-based film (using PET as substrate).</li> <li>• 5 different structures of OLED with distinct number of graphene layers are made, including:               <ul style="list-style-type: none"> <li>- Only PET (no encapsulation film),</li> <li>- PET/PDMS,</li> <li>- PET/2-layered graphene/PDMS,</li> <li>- PET/4-layered graphene/PDMS, and</li> <li>- PET/6-layered graphene/PDMS.</li> </ul> </li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <ul style="list-style-type: none"> <li>• It is confirmed that MgO/S-H nanocomposite at 4.5 dyads had the lowest WVTR reading which is <math>4.33 \times 10^{-6}</math> g/m<sup>2</sup>/day.</li> <li>• At 60 nm of MgO, the WVTR value is <math>5.83 \times 10^{-2}</math> g/m<sup>2</sup>/day and <math>7.13 \times 10^{-2}</math> g/m<sup>2</sup>/day at 40 nm of MgO.</li> <li>• This comparison test result demonstrated that the thicker encapsulation layer only slows down the permeation of water vapor into the OLEDs.</li> </ul>                                                                                                                     | [95] |
| 1) Magnesium oxide (MgO)<br>2) Silica nanoparticle-embedded hybrid (S-H) nanocomposite          | 1) MgO = 0.04<br>2) S-H = 0.2                                         | 1) ALD for MgO deposition<br>2) Spin-coating for deposition of S-H nanocomposite               | <ul style="list-style-type: none"> <li>• The resistance measurement is taken at 30 °C, 90% RH with voltage supply of 20 mV</li> <li>• Different values of dyads of MgO/S-H nanocomposite are utilized (1.5, 2.5, 3.5 and 4.4 dyads).</li> <li>• A comparison test is also done by comparing the WVTR outcome of 60 nm with 40 nm of MgO.</li> <li>• The encapsulation layer is fabricated by layering the LiF and photoresist in a sequence (LiF/photoresist/LiF). Then, the layer is enclosed with a Cu foil.</li> <li>• 8 V is utilized during the luminance test.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <ul style="list-style-type: none"> <li>• The results revealed that the dark spots are occurred within 1 week after the OLEDs operation. This record is comparable with the glass-lid encapsulation.</li> <li>• No remarkable difference in the formation of dark spots is recorded.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                 | [96] |
| 1) Lithium fluoride (LiF)<br>2) AZ1512-photoresist polymer (photoresist)<br>3) Copper (Cu) foil | 1) LiF = 0.6<br>2) Not stated for photoresist<br>3) Cu foil = 60      | 1) Thermal evaporation method for LiF deposition<br>2) Spin-coating for photoresist deposition | <ul style="list-style-type: none"> <li>• The moisture permeation rate is taken at 37.8 °C, 100% RH.</li> <li>• The encapsulation layer is fabricated by layering the Al film onto the layer of Polyacrylate-based adhesive.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | <ul style="list-style-type: none"> <li>• The L-V characteristic between before and after the encapsulation process showed a similar feature with the non-encapsulated OLEDs.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | [97] |
| 1) Polyacrylate-based adhesive<br>2) Aluminum (Al)                                              | 1) Polyacrylate-based adhesive = 15<br>2) Al = 185                    | Conventional lamination process                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | [98] |

employed as the encapsulation films, layered on top of the cathode structure. Concisely, the result revealed that the performance of the OLED samples is enhanced with the increment in the encapsulation film thickness.

Until now, abundant of encapsulating techniques have been proposed and developed such as hermetic encapsulation technique by using glass tube, epoxy resin and nitrogen gas. However, the overall thickness of an OLED is still greatly affected by these encapsulation techniques, making them not preferable by the OLED's manufacturers. To encounter this matter, thin-film encapsulation (TFE) technology has been introduced and frequently been chosen due to abundant of benefits such as produced a thin, durable and lightweight encapsulation layer. On top of that, TFE is the most effective technology in producing an excellent encapsulation layer that acts remarkably as a shield towards the water vapor and oxygen infiltration into the OLEDs [84]. The thin films encapsulation can be deposited by a number of different methods such as sputtering, thermal evaporation, chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition or by atomic layer deposition (ALD).

In common practice, ALD is a widely used technique in TFE technology and is considered as one of the best candidates to produce a high-quality thin film layer for encapsulation purpose [85]. The main advantages of this approach are including an accurate thickness control at the Ångström (Å) and monolayer level [86] which produced a greatly uniform and conformal, as well as a densely packed film even on large and complex surfaces. In addition, ALD also offers a feature of eliminating surface defects such as pinholes, tiny cracks and asperities in the encapsulated thin film [87]. Thus, a film integrity can be assured.

Most of the time, ALD method is associated with aluminum oxide or alumina ( $\text{Al}_2\text{O}_3$ ) as the material for the encapsulation process [88]. However, high deposition temperatures (usually above the glass transition temperature of the materials used) will be employed during the fabrication process. This is an atrocious news since organic layers of OLED are highly sensitive to heat and they demand ALD with low-temperature process in order to deposit  $\text{Al}_2\text{O}_3$  onto the OLED's substrate.

In 2015, Li et al. [89] have performed an experiment by using ALD method on the Si substrate at both 80 °C (low temperature) and 200 °C (high temperature). Succinctly, the authors have manipulated the pumping gas time during the  $\text{Al}_2\text{O}_3$  preparation process, where the pumping gas time is 30 s and 10 s, respectively at 200 °C and 80 °C. The results are remarkably showed that the water contact, film surface roughness and the corresponding surface energies for the tested OLED are both virtually similar. Li and co-workers also added that – by adjusting the pumping time, any unsolicited reactions and the formation of cavities that allow the water and oxygen penetration can be eliminated. Thus, it is proved that the ALD process in organic electronic devices at low temperature can be achieved.

Many researchers have been implementing the ALD technique broadly, since this particular approach is one of the most affable processes, especially towards the organic materials used in OLEDs by which lead to a better improvement in encapsulation technology. Moreover, ALD method has enabled Lin et al. [90] to deposit the zinc oxide (ZnO) and  $\text{Al}_2\text{O}_3/\text{ZnO}$  layer as the encapsulation film on their OLED samples at a low temperature of 70 °C. At the same year, Zhang et al. [91] have hybridized the inorganic and organic materials to be used as the encapsulation film on OLEDs by using ALD method, deposited at 85 °C. Different numbers of hybrid encapsulation layers are tested. As shown in Fig. 16, they are including (1) a single layer of alumina ( $\text{Al}_2\text{O}_3$ ), (2) a hybrid layer of alumina and zirconium dioxide ( $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ), (3) a hybrid layer of alumina, zirconium dioxide and aluminum alkoxides with carbon-containing backbones ( $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{alucone}$ ) and (4) three pairs of  $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{alucone}$  layers.

The authors have discovered that the three pairs of hybrid encapsulation layers of  $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{alucone}$  structure have the best barrier performance with water vapor transmission rate (WVTR) at 25 °C

and 85% RH is as low as  $8.5 \times 10^{-5} \text{ g/m}^2/\text{day}$ . According to Zhang et al., the three pairs of inorganic/organic hybrid layers showed an exceptional barrier performance as compared to other layers is due to a great densification between the inorganic/organic layers. This is because the rate of water vapor infusion into the OLED devices is highly influenced by the density of the material. Furthermore, the time taken for gases diffusivity is increased since the permeation path has become longer by the presence of the organic layer (alucone). At the same time, the alucone layer acted chemically by entrapping the water vapor atoms which eventually resulted in the decrement of diffusivity speed of water vapor into the OLED structure.

Nevertheless, the encapsulation layer is only capable to decelerate the penetration of humidity and moisture into the OLEDs at a certain period of time. Based on the literatures done, several studies on the materials suitability and their quality as a coating barrier have proved that the encapsulation layer managed to prevent the permeation of water vapor into the encapsulated OLEDs, but at a restricted time only as shown in Table 5. Ultimately, detrimental events will still be triggered within the OLEDs structure and resulted in the formation of dark spots. On top of that, the permeation process highly depends on the materials employed in order to manufacture OLEDs. Therefore, by gaining some understandings in the formation mechanisms of dark spots will significantly benefit the manufacturers and electronics research communities globally in order to extricate the low stability and short lifetime problem in OLEDs.

## 5. Conclusion

In OLED's development, the local non-emissive area or well-known as dark spot is an intricate setback to produce a superior OLED for long-term commercial success. The formation of dark spot is always associated with the failure of OLED due to poor environmental stability of the devices even when the devices are fully encapsulated. However, the definite root cause of dark spots formation and their growth mechanisms are still remain as a concern subject. Based on the literatures reviewed, the two root causes of formation mechanisms are projected which are the presences of foreign impurities and pinholes, as well as high electric current intensity.

The foreign impurities are frequently introduced during the fabrication process. Due to shadow effects, tiny pinholes are created on top of the OLED surface. Eventually, these pinholes provide a pathway for the water vapor, moisture and oxygen to penetrate into the OLED layers and induced further catastrophic events such as oxidation process,  $\text{Alq}_3$  hydration, hydrogen gas evolution and delamination of cathode. These processes will gradually lead to the OLEDs failure.

In addition, the discrepancy of the electrons reachability within the OLED layers is mainly caused by the presence of short circuits and the variability of surface roughness of the OLED layers. Temperature will be generated locally and elevated heat will be produced afterwards. As a consequence, electro-migration, crystallization of TPD layer and decomposition of organic layers into volatile products will occur which leads to the dark spots growth. By understanding the root cause formation of dark spots mechanisms in OLED comprehensively, it will definitely provide a better knowledge for further improvement in OLED applications.

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