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Film Properties and Polycrystallization of Organic Dyes on ITOs with Surface Treatment for Organic Light-Emitting Diodes

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SUMMARY

ITO (indium tin oxide) has now been widely used as the transparent anode for organic light-emitting devices (OLEDs). We used various methods of ITO surface treatment and examined their effects by measuring contact angle and calculating surface energy. We also prepared OLEDs with ITO treated by each method, and estimated their characteristics. The surface of ITO treated by UV-O_3 or O_2-plasma was more hydrophilic than that treated by only organic rinse or no treatment, and consequently the characteristic of the OLED was improved. We suppose these treatments affect the hole injection from ITO into the organic layer, due to ionization potential or surface cleanness. We also investigated the time degradation of NPD films on the ITO substrates. The films deposited with a high deposition rate polycrystallized faster. © 2006 Wiley Periodicals, Inc. Electr Eng Jpn, 156(4): 1–8, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/eej.20379

Key words: organic light-emitting diode; indium tin oxide; surface treatment; contact angle; polycrystallization.

1. Introduction

Organic EL [1] offers the advantages of thinness, light weight, wide visual field with self-emitted light, fast response time, and the possibility of creating flexible displays. As a result, they are expected to play an active role as next-generation display devices. In an organic EL element, a carrier is injected into the organic layer from an electrode, and is rejoined in the light-emitting layer after transport, and then light is emitted. Because organic materials are ordinarily insulators, the state of the boundary between the electrode that performs the carrier injection and the organic layer has a considerable effect on the efficiency of light emission. The authors have performed an evaluation on this boundary phenomenon for organic layers using an ITO (indium tin oxide) substrate, widely used as an anode material because of its high transparency and conductivity. The authors evaluated how the characteristics of the organic EL element created using an ITO surface and substrate vary by performing surface processing on the substrate. They also evaluated the aggregation rate of an organic thin film on a substrate using a separate manufacturing method.

2. Experimental Methods

In this research the authors used three types of ITO: an sp-ITO manufacturing a three-container process and spatter film formation for the positive pole substrate (note that this is not the most current organic EL substrate), Super ITO as manufactured by ULVAC, and EB-ITO, manufacturing using electron beam deposition film formation from Matsuzaki Shinku (now Geomatics). For the substrate cleaning method, the authors used organic purificiation [deionized water/ultrapure water (twice)/acetone (twice)/2-propanol (twice) each for 5 minutes of ultrasonic cleaning], then UV ozone processing, and O_2 plasma processing. The UV ozone processing was performed using a Nihon Laser Electronics UV-O_3 cleaner, and the O_2 plasma processing was performed using a Sanyu Electronics Desktop Quick Coater SC-701.

Furthermore, the organic EL used in this research was manufactured in a 2 to 5 × 10^{-6} Torr vacuum using the vacuum deposition method with a copper phthalocyanine (CuPc) as the hole injection layer, the diamine derivative (NPD) as a hole transport layer, and the tris (8-hydrooxyquinoline) aluminum (Alq3) as the light-emitting layer, and a LiF as the electron injection layer and Al used as the negative electrode metal. Element structure: ITO [150 nm]/CuPc [30 nm]/NPD [50 nm]/Alq3 [50 nm]/LiF [0.6 nm]/Al [~ 200 nm]. The current–voltage measurement

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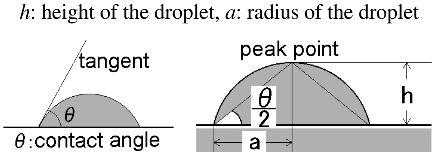


Fig. 1. Contact angle measurement.

was taken by adding a step voltage (rate of voltage increase: 0.5 V/s) to the sample material using a source measure unit (238 Source Measure Unit, Keithley), and then intensity was measured using a luminescence meter (BM-8, Topcon). The transmitted spectrum measurement was performed with a photospectrometer (U-3000, Hitachi), and the observation using a polarizing microscope was performed with a transmission-type polarizing microscope (Optiphot-2, Nikon). The ionized potential (Ip) was measured using a photoelectron spectrometer (AC-2, Riken Keiki), and the surface roughness of the substrate and film was measured using AFM with SPM (SPA 3000, Seiko Electronic Industries). The test materials were kept in the dark and stored in a 1×10^{-1} Torr vacuum.

The authors used contact angle measurements to evaluate the surface status of the substrate. The measurements were performed using an automatic contact angle meter (CA-VP type from Kyowa Kaimen Chemical). As can be seen in Fig. 1, the contact angle is the angle formed between a tangent to the water droplet when it drops on the substrate and the substrate itself. In this research, the average value from 10 measurements taken with ultrapure water was used. The contact angle was found using the θ/2 method. Because 2 μl of water was dropped, the shape of the droplet should represent a portion of a sphere. As a result, the following equation holds:

$$\tan(\theta/2) = h/a \tag{1}$$

Thus, the contact angle can be found as follows:

$$\theta = 2\tan^{-1}(h/a) \tag{2}$$

3. Results and Discussion

3.1 Measurement of the contact angle

Because the surface state of the ITO in direct contact with the organic layer has a significant effect on the elemental properties, the authors evaluated the effects of differences in surface treatment methods on the anode surface and the elemental properties. Further, they used Super ITO, which is smoother, in order to perform a comparison with a sp-ITO substrate.

The results of measuring the transmission spectrum in ITO substrates subjected to organic washing or plasma treatment showed virtually no changes in the transmission spectrum when the plasma treatment time was between 0 and 2 minutes, but when treatment took 5 minutes, the permeability increased over preprocessing. This shows that the plasma treatment results in the ITO being etched by plasma particles if treatment exceeds 5 minutes.

The contact angle is small, as can be seen in Fig. 2, when the ITO substrate is subjected to surface treatment using these methods. Given that an unwashed sample has a large contact angle, this suggests that there are organic oils on the surface. The value of the contact angle decreases as organic washing, ozone treatment, or plasma treatment are performed, as can be seen in Fig. 3. Although the contact angle decreases as the treatment time increases, at some point the value reaches saturation. Moreover, among the substrates, Super ITO has a smaller value when organic washing or ozone treatment is performed. During the process of humidity washing, first, hydrophilic dirt and large bits of dust are removed from the substrate, and then absorbent materials which are hydrophobic and larger bits of dust on the substrate are removed by the water. Ozone treatment and plasma treatment eliminate carbon dioxide and water by oxidative decomposition of organic molecules remaining on the substrate surface after organic washing. In addition, in plasma treatment a direct impact effect is achieved on organic molecules as a result of the etching effect. As a result of these processes, the impurities are removed from the substrate surface, and a highly hydrophilic ITO surface results, so the contact angle is small. On the other hand, the contact angle for organic materials is large compared to a washed substrate. The surface energy can be represented as a function of cos θ [2]. As a result, a small contact angle means that the surface energy is high.

Water is used when measuring the contact angle. Consequently, the smaller the contact angle, the greater the wettability with respect to water, and the greater the hydrophilic properties. When letting a droplet of oil fall on the surface of water, the oil collects, moves on the water's

non-treat., organic-washing, organic-washing+ozone-treat.(10min.), organic-washing+plasma-treat.(2min.)

Fig. 2. Photographs of water droplets on ITO substrates (sp-ITO).

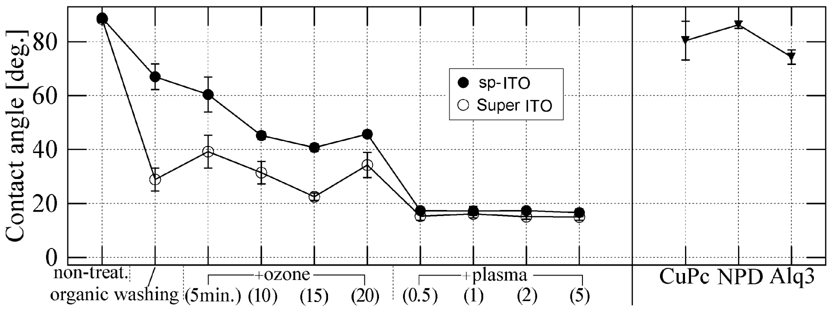


Fig. 3. Contact angles of surface-treated ITOs and organic materials.

surface and gathers itself somewhere without mixing with the water. In the same fashion, when forming a thin film on a substrate, if the effect of the surface energy, the basis for the value of the contact angle, is large, then a uniform film will be difficult to form when the difference in the contact angle for the substrate and the thin film material is substantial.

When fabricating devices, there seems to be some form of time lag from when treatment starts to when the deposition device is reached. As a result, the authors measured how the contact angle changed as a result of leaving the substrate alone after treatment. As can be seen in Fig. 4, when the substrate is left alone after treatment, the value of the contact angle steadily rises, and the standard deviation also increases. This suggests that if the substrate is moved to a film manufacturing device in a short time after treatment, the probability of an effect on film manufacture is lower.

By performing surface treatment to the substrate, the value of the contact angle on the substrate surface is reduced, and wettability is improved. This is extremely useful when using the printing method currently mentioned as one efficient manufacturing method for devices. Moreover, an effect of O_2 plasma treatment is that, as can be seen in the ESCA measurements of the chemical composition of the ITO substrate surface after plasma treatment shown in Table 1, the C atoms (depending on the organic molecules absorbed onto the substrate surface) decrease in number, and the O atoms increase. As a result of treatment, the ITO oxygen defects are reduced, and the composition (In:O = 2:3) of oxidized indium (In_2O_3) is approximated. Figure 5 shows the ionization potentials (Ip) for the materials used in the ITO substrate and organic layers subjected to the various forms of treatment. An increase in the substrate Ip as a result of treatment was seen in the Super ITO. The small change in the Ip of the sp-ITO is currently under evaluation. Based on these results, the surface treatment of an ITO substrate can be seen as causing the elimination of the residual organic molecules in the substrate surface, an increase in the amount of oxygen in the surface, and an increase in the hole injection that accompanies a decrease in the injection barriers due to the rise in Ip, depending on the substrate.

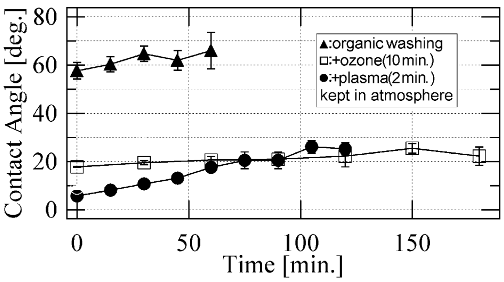


Fig. 4. Time dependence of contact angles of surface-treated ITOs (sp-ITO).

3.2 Observations over time of the thin films

As for degradation over time of the devices, one primary cause is the condensation and polycrystallization of the organic materials formed on the thin film. In order to evaluate the differences in the form of polycrystallization resulting from the surface state of the substrate, the authors used a polarizing microscope to observe the progress of polycrystallization after a 50-nm NPD thin film was deposited on an ITO substrate. In order to investigate the effects of the surface roughness of the ITO, three types were compared: Super ITO (calculated average roughness, Ra =

Table 1. Comparison of chemical compositions of ITO surface using ESCA

	ITO compositions[%]			
	In(In/In)	Sn(Sn/In)	O(O/In)	(C/In)
non-treat.	45.9 (100)	3.3 (7.3)	50.8 (111)	(209)
plas.	36.9 (100)	3.1 (8.2)	60.0 (163)	(101)

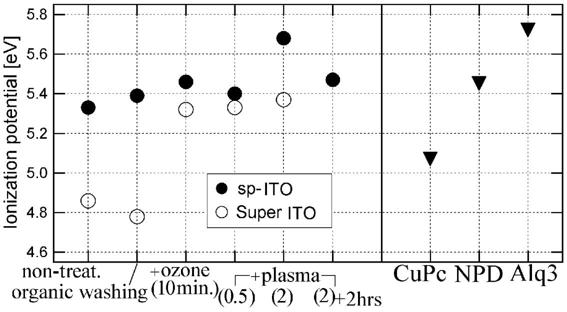
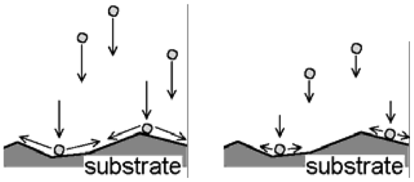


Fig. 5. Ionization potentials of surface-treated ITOs and organic materials.



left:high depo-rate・smooth, right:low depo-rate・rough

Fig. 7. Image of NPD film polycrystallization.

1.1 nm), sp-ITO (2.7 nm), and EB-ITO (4.0 nm), and the authors evaluated cases in which the deposition rate was normal (0.2 nm/s) and tenfold (2 nm/s). The ITO substrate was subjected to 10 minutes of surface treatment consisting of organic washing and ozone treatment. As can be seen in Fig. 6, the greater deposition speed (d) through (f) represents a greater number of polycrystallization regions (equals faster growth of polycrystals), and the number of crystals is larger for (c) with its lower deposition rate because the EB-ITO substrate had the greatest surface roughness. There was virtually no change over time seen in the number of crystals. This is thought to be an effect of nucleus formation on the substrate during deposition, resulting from differences in the substrate. As can be seen in Fig. 3, the difference in the contact angle for ITO and NPD is large, and the adhesive force is small. As a result, the molecules at the start of deposition readily move on the substrate, as can be seen in Fig. 7. Consequently, film reformation occurs, and in the case of (c), the kinetic energy of the molecules is low, and the effects of roughness on the substrate cannot be ignored. As a result, the molecules condense in groups without moving much, and so there are a large number of condensation points, and a large number of polycrystals. On the other hand, at the high-deposition rate, the roughness in the film surface becomes larger, clustering occurs in the gas phase, and as a result, the film has a lot of gaps, as can be seen in Fig. 8. Another possible cause is that external factors such as water readily have an effect because the surface area is large and the molecules are using the gaps to move. Moreover, when an NPD thin film of 100 nm was tested, the growth of polycrystallization was a bit slower. The molecules near the boundary have more difficulty moving due to the weight of the NPD layer on top, and so the growth rate of polycrystallization is thought to be slower. When introducing a CuPc layer (30 nm) between the ITO and NPD, the growth rate of polycrystallization is overall a bit slower (Fig. 9, left). This seems to mean that the adhesive force is stronger and polycrystallization is less likely to occur as a result of the

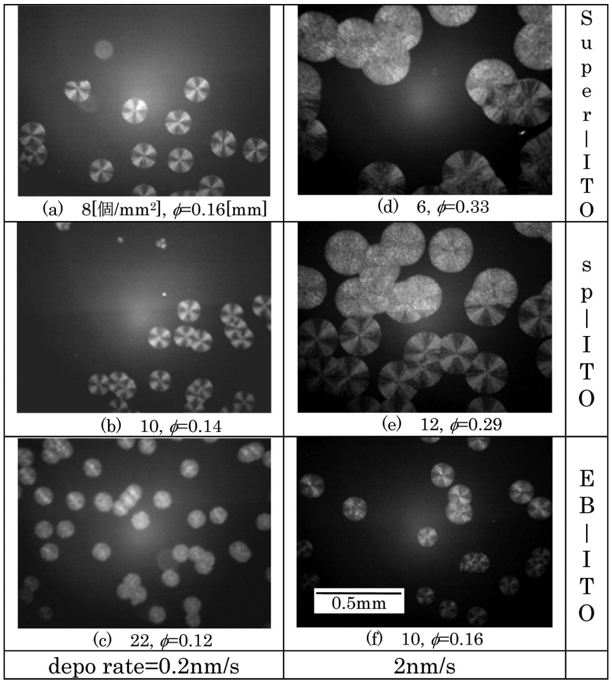
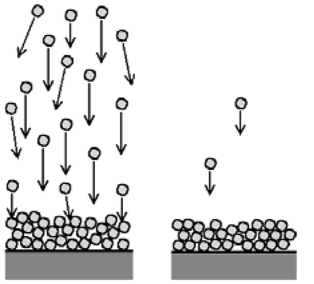
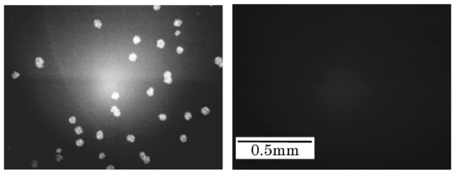


Fig. 6. Polarized photographs of NPD films on ITOs (ITO/NPD [50 nm]).



left:high depo-rate, right:low depo-rate

Fig. 8. Image of NPD film polycrystallization.



left : ITO / CuPc / NPD, 5 days after preparation
right : ITO / NPD / Alq3, 118 days after preparation

Fig. 9. Polarized photographs of NPD films on sp-ITO.

value of the contact angle being close to the NPD due to the ITO, and the CuPc representing a boundary with the NPD. On the other hand, when Alq3 (50 nm) is deposited on the ITO/NPD, the growth rate of polycrystallization is much slower compared to the other cases (Fig. 9, right). This is thought to be because the Alq3 layer eases the external effect due to the NPD layer being inverted by the Alq3 layer, in addition to the effects described above. Because the rate is very slow, the effects of polycrystallization cannot be denied in the upper portion of the thin film.

3.3 Element properties

The initial properties of the elements created using ITO either left unwashed or subjected to 10 minutes of organic washing, or organic washing and ozone treatment are as seen in Figs. 10 (sp-ITO) and Fig. 11 (Super ITO). In terms of current efficiency for the devices, values close to those found for ozone treatment were obtained even for no washing. This is thought to represent an increase in efficiency as a result of improving balance with electron injection on the cathode side and hole injection when no washing is performed being suppressed. Because hole injection is suppressed, this is not practical because the driving voltage rises, and the light-emitting surface is not uniform and has numerous dark spots. Properties virtually identical to sp-ITO and Super ITO were obtained after 10 minutes of organic washing and ozone treatment.

In sp-ITO, the initial properties for devices subjected to 10 minutes of organic washing and ozone treatment, and then 30 seconds of organic washing and plasma treatment are as shown in Fig. 12, and are almost the same. Given this,

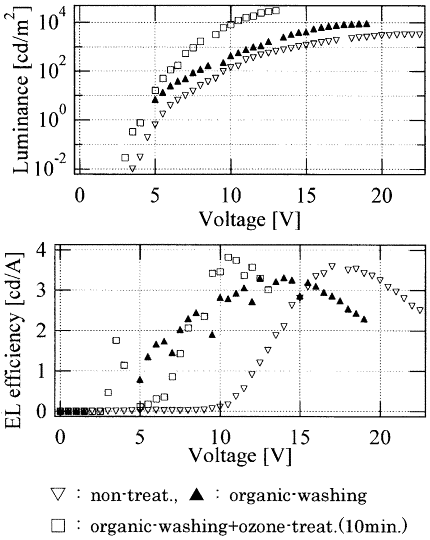


Fig. 11. EL properties of OLEDs (Super ITO).

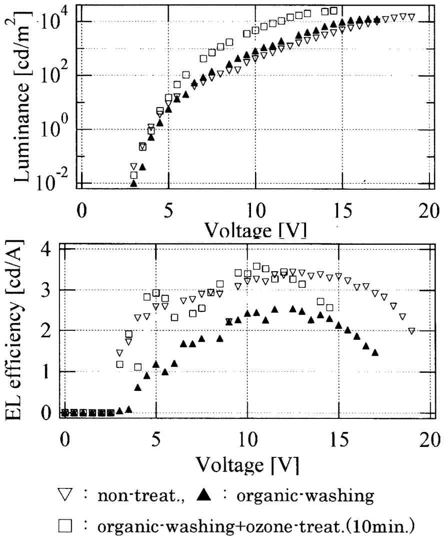


Fig. 10. EL properties of OLEDs (sp-ITO).

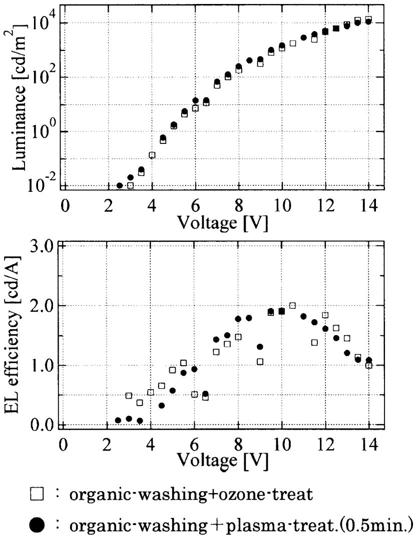


Fig. 12. EL properties of OLEDs (sp-ITO).

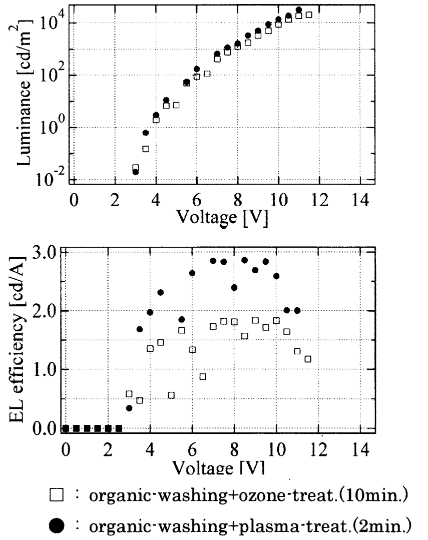


Fig. 13. EL properties of OLEDs (sp-ITO).

plasma treatment is more effective in a shorter time based on a simple comparison of treatment time. On the other hand, when the plasma treatment time was extended to 2 minutes, properties better than organic washing and ozone treatment for 10 minutes were obtained, as can be seen in Fig. 13. Thus, plasma treatment is effective in a short time, and can be considered as a treatment method with better properties than ozone treatment even when the treatment time is extended.

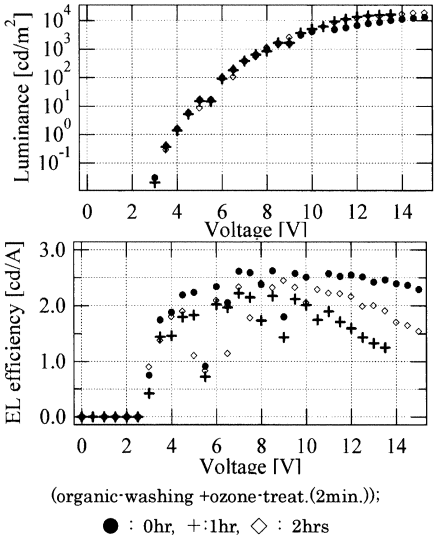


Fig. 14. EL properties of OLEDs after keeping in an atmosphere of sp-ITO.

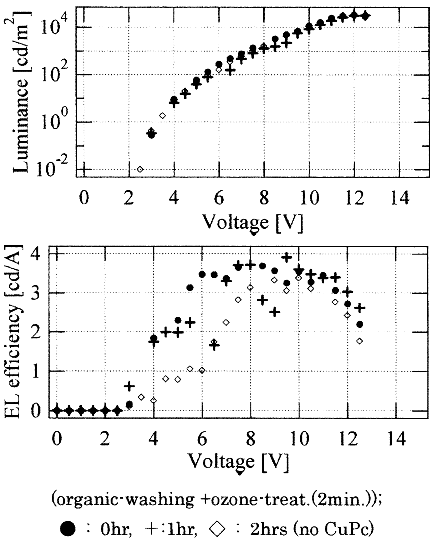


Fig. 15. EL properties of OLEDs after keeping in an atmosphere of sp-ITO.

Using plasma treatment, devices with properties similar to those of ozone treatment for a brief time can be created, and devices with better properties can be created by varying the treatment time. As a result, plasma treatment can be seen as a treatment method that offers improvements in device properties. In addition, because of good phase characteristics throughout the vacuum process during device manufacture, the plasma treatment is widely used. On the other hand, the difference in the contact angle between the ITO and the organic materials increased and device properties improved when performing this treatment.

The initial properties of devices manufactured using an sp-ITO substrate left for 0, 1, or 2 hours in the atmosphere after 2 minutes of organic washing and plasma treatment are shown in Fig. 14. Even when an ITO substrate left in the atmosphere was used, large changes such as in device efficiency were not seen. Film formation on a CuPc layer on the ITO is expected to be significantly different from that of NPD, and the use of the CuPc layer should greatly contribute to improvements in the device properties. As a result, Fig. 15 shows a comparison of creating devices without using CuPc. In this instance, the rise in the current efficiency was slower in the substrate left for 2 hours in atmosphere as compared to the others, a result different from what was seen in the previous section. Given this, in devices that do not use CuPc, if they are left for 2 hours in the atmosphere, the injection in holes seems to be blocked. Thus, based on this result as well, substrates should be moved to film manufacturing devices within a short time after treatment.

4. Conclusion

In this research, the authors evaluated the state of the organic layer boundary and the transmission anode substrate. By performing surface treatment of the substrate, the authors reduced the value of the contact angle with the substrate surface, increased the ionization potential, and as a result improved element properties. In particular, major changes were seen in the Super ITO. Given this, the UV ozone treatment and O_2 plasma treatment can be seen as effective methods for ITO substrate surface treatment used for organic EL. Moreover, because the process and phase characteristics when manufacturing devices and the effect of a short time period for O_2 plasma treatment in particular are good, this is a superior treatment method. The improvements in device properties due to treatment have various effects, including the elimination of residual matter from the ITO substrate surface, changes in the chemical composition, and an increase in the ionization potential. Moreover, with respect to the progress of polycrystallization due to the passage of time on an NPD film manufactured on an ITO substrate, the number of crystals is affected by the ease with which the molecules that accumulate initially upon deposition can move, and the growth rate polycrystallization is affected by the ease with which molecules can move on the film overall (in particular on the upper surface). On the other hand, the value of the contact angle was steadily improved and the device properties deteriorated as the substrate was left in the atmosphere after surface treatment. Although the range of time over which a substrate is left in the atmosphere during the typical manufacturing process has no significant impact on the device properties, it is clear that moving the substrate to the deposition step rapidly after treatment is beneficial.

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