Development of Low Damage Sputtering Process for OLED Devices

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Organic light emitting diode (OLED) devices are applied to various displays such as smartphones, monitors, and TVs, but it is necessary to improve the cost and lifetime of such displays. Top emission type OLEDs have high light extraction efficiency but require higher transmission and lower resistance cathode electrodes, so we have developed a low damage sputtering process for these OLED devices.

Sputtering processes with high temperatures and lots of particles not only reduce device performance, but also reduce mass production yields. That is why ULVAC's sputtering process concepts for these OLED devices are "low damage," "low temperature," and "low particle."

In this paper, we analyzed the sputtering damage factor related to device performance and established a sputtering process that can reduce the damage factor. The drive voltage and efficiency of OLED devices using the low damage sputtering process was the same as that of the reference vapor deposition device, and the lifetime was more than 20% longer.

1. Introduction

Organic Light Emitting Diodes (OLEDs) are widely used not only for small- and medium-sized displays such as smartphones and monitors, but also for large displays such as TVs, signage, and recently, walls, which take advantage of their high-resolution and flexible characteristics.

OLED devices, invented by C. W. Tang and S. A. Vanslyke in 1987,[1)] are devices formed by the sequential vacuum vapor deposition, on an indium tin oxide (ITO) substrate, of diamine, which acts as the hole-transport layer, an organic material called tris(8-hydroxyquinolinato)aluminum (Alq_3) as the electron-transport and light-emitting layer, and MgAg as the cathode electrode. The development of OLEDs was stimulated by the realization of high current efficiency and brightness in thin films on the order of 100 nm that could be driven at voltages as low as 5V.

In subsequent OLED development, development in search of more efficient device performance progressed separately for light-emitting materials and functional films as the functionalities constituting OLED devices. In the case of light-emitting materials, the potential of OLED displays was demonstrated by Idemitsu Kosan Co., Ltd.'s development of a blue light-emitting material[3)], which had presented significant challenges in terms of performance and lifetime compared to red and green, the other primary colors of light.

When the organic material is excited, 25% of the material enters the singlet state and 75% enters the triplet state, and the light produced during the return to the ground state is called fluorescence and phosphorescence, respectively. Although phosphorescence can achieve high luminous efficiency[4)], it is disadvantageous in terms of cost because it uses rare metals such as iridium and platinum. In recent years, however, further material development, including materials using thermally activated delayed fluorescent (TADF)[5)] and technology using TADF[6)], has greatly improved performance, achieving high energy conversion efficiency without the use of rare metals.

The technology to form low-molecular-weight organic materials by a vapor deposition process came first, followed by the technology to form polymer organic materials by dissolving them in solution and coating/printing them on the necessary areas. Today, high-performance OLED displays are indispensable in a wide variety of fields.

With a large share of the sputtering manufacturing equipment market in the field of flat panel displays (FPDs), ULVAC has been developing sputtering technology applicable to OLEDs, which are expected to be larger in size, higher in performance, and lower in cost going forward.

2. OLED technology

2.1 OLED displays

Table 1 is an item-by-item comparison of OLEDs versus liquid crystal displays (LCDs). OLEDs are self-luminous

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displays and do not require a backlight unit like LCDs. This gives OLEDs the advantages of high contrast and being applicable to thinner, more lightweight, and more flexible devices compared to LCDs. Today, foldable and rollable OLED displays are making a splash in the market. However, OLEDs are inferior to LCDs in terms of cost and lifetime, and improvements are needed to further expand their use and market share.

2.2 OLED configuration

The configuration of a typical OLED device is shown in Fig. 1. Holes are injected from the anode electrode and electrons from the cathode electrode, and light is emitted when the holes and electrons recombine in the emissive layer (EML). At that time, in order to inject and recombine holes and electrons more efficiently, the following functional films, among others, are allocated as necessary: a hole injection layer (HIL), hole transport layer (HTL), electron blocking layer (EBL), hole blocking layer (HBL), electron injection layer (EIL), and/or electron transport layer (ETL).

Fig. 2 shows (a) top emission type and (b) bottom emission type OLED devices. In the bottom emission method, where light is extracted through a thin film transistor (TFT) circuit, the aperture ratio is inevitably small because it is limited by the TFT circuit. The top emission method, on the other hand, has the advantage that there is nothing to block the light, resulting in high light extraction efficiency and long lifetime with low power consumption.

Furthermore, OLED devices utilizing a microcavity structure have made it possible to obtain purer red, green, and blue (RGB) colors and light emission with stronger intensity, as reported by Takata et al.[7]. In order to obtain a stronger resonance effect, the optical design between the electrodes can be optimized individually for R, G, and B.

Table 1 Comparison list of OLED and LCD displays

Items	OLED	LCD
Luminance	Good	Good
Contrast	Excellent	Good
Response	Good	Fair
Power consumption	Fair to Good	Good
Flexibility (Thin film)	Good	Poor
Lifetime	Fair	Good
Cost	Fair	Excellent

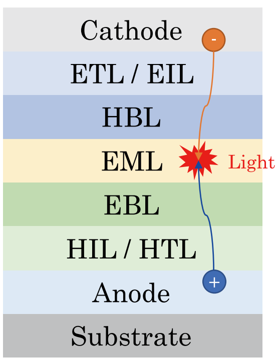

Fig. 1 Configuration of typical OLED device

2.3 OLED manufacturing method

At present, the manufacturing method of OLED devices is mainly divided into two categories, as shown in Fig. 3.

First, Fig. 3(a) shows an OLED device made using the RGB coating method commonly used in smartphones and small- and medium-sized monitors, also known as the side by side (SBS) method. R, G, and B are individually formed by using vapor deposition and printing techniques. For SBS-type OLEDs manufactured by vapor deposition, an ultra-thin metal mask with a precise array of microscopic holes is used to limit the deposition area on the substrate. Although SBS is well established as a technology for forming high-resolution

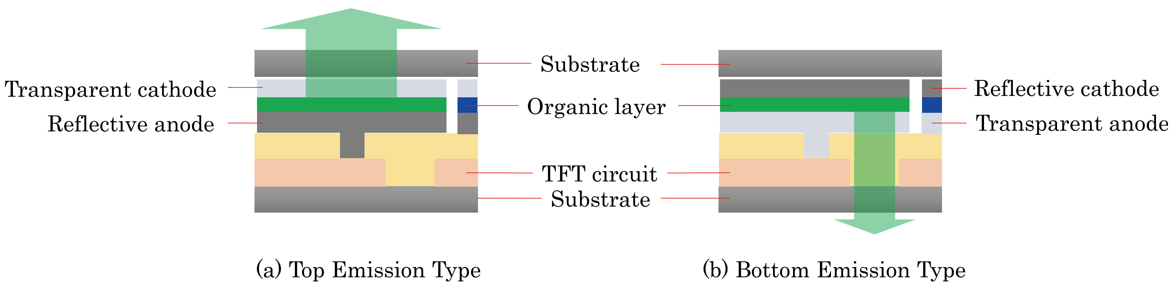

Fig. 2 Top and bottom emission type OLED devices

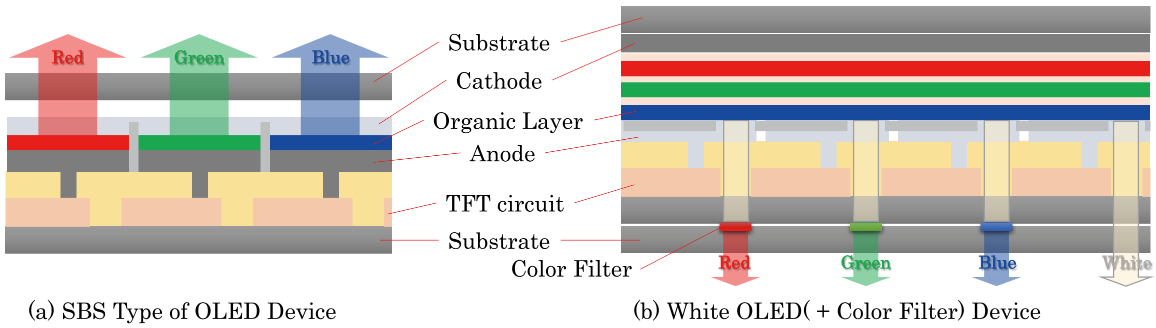

Fig. 3 OLED device structure

displays, it requires the fabrication of precision masks and techniques for high-precision alignment of mask and substrate. For SBS-type OLEDs manufactured by printing technology, on the other hand, printing is performed in an atmospheric environment and does not require expensive vacuum equipment, which is advantageous for large-scale production. Theoretically, it is possible to deposit only the necessary organic materials on the substrate, thereby improving material usage efficiency. However, it is essential to control and precisely drop a solution with a very small amount of dissolved organic material by means of a printing head and to dry it uniformly.

Fig. 3(b) shows the method in which a white OLED is formed by stacking R, G, and B light-emitting layers by means of a vapor deposition process, and then color filters are used to produce the RGB colors. Unlike the vapor deposition SBS OLEDs, no precision metal mask or alignment is required. This method has a high market share for large OLED displays such as TVs and signage. However, since the materials to be stacked are not only the R, G, and B light-emitting layers, but also the functional films described above, large-scale vapor deposition equipment is required. Furthermore, passing the light through color filters reduces the light extraction efficiency.

3. Development of low damage sputtering process for OLEDs

3.1 Need for a low damage sputtering process

The structure of OLED devices is expected to shift from the bottom emission type to the more efficient top emission type. Conventionally, the cathode electrode has generally been formed from Al, Ag or an Ag alloy by a vapor deposition process. However, as displays become larger, there is a need for cathode electrodes with higher transmission and lower resistance. ITO and indium zinc oxide (IZO), which are commonly used as transparent conductive oxides (TCOs), are also widely used materials for devices such as FPDs and solar cells. To obtain good TCO film quality by vapor deposition, a high-temperature process is required, which is not suitable for OLEDs. However, with sputtering technology, it is possible to form TCOs with low resistance and high transmission while maintaining a low substrate temperature. However, when the TCO material is deposited by sputtering on the cathode electrode of a top emission type structure, there is a risk of damage to the underlying organic film, which is why it is necessary to develop a low damage sputtering process for OLED devices.

3.2 Process concepts

ULVAC's process concepts for OLED devices are "low damage," "low temperature," and "low particles." In OLED devices, it is believed that there are multiple factors that contribute to damage caused by sputtering, and the development and evaluation of low-damage processes have been pursued by many researchers over time[8-14]. However, it is difficult to identify a single cause of damage. In other words, the damage factors and effects differ depending on the device, structure, and material, suggesting the need for careful investigation. In the production of OLEDs, when depositing films by sputtering, it is necessary to use thin metal masks with thicknesses in the order of μm to demarcate the deposition area from the non-deposition area. It is preferable to keep the substrate temperature below 80°C because higher temperatures may cause not only damage to the organic materials but also deformation of the mask, which may worsen the product yield. The same goes for particles. Particles that fall on the OLED device or OLED element degrade the performance of the device[15] and cause defects when sealing the device. Therefore, when considering sputtering processes applicable to OLEDs and the development of mass production processes, it is necessary to consider not only the damage caused by sputtering, but also the temperature and particles.

3.3 Evaluation system

The SCH-135 sputtering system used for the OLED evaluation is shown in Fig. 4. It is a horizontal in-line type sputtering system. During production, substrates are continuously transported from the loading chamber to the unloading chamber while being sputtered, which gives the system superior productivity with a minimal footprint. Fig. 5 shows a cross-section image of the rotary cathode used for the OLED device evaluation. The cylindrical target material is IZO doped with 10.7 wt% zinc oxide. A magnetic circuit is built into the bonded backing tube for cooling the target, and a high-density plasma is formed in the vacuum atmosphere along the magnetic field lines emitted from the magnetic circuit. By rotating the target during discharge by sputtering, the target can be eroded uniformly and high material usage efficiency can be obtained. We used this evaluation system and rotary cathode to evaluate the OLED devices.

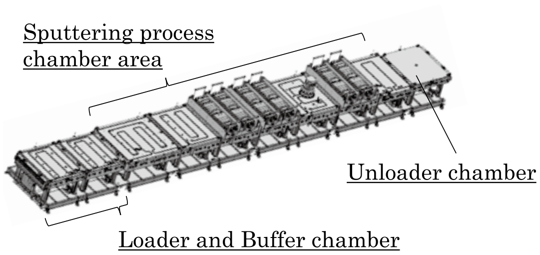

Fig. 4 SCH-135 system

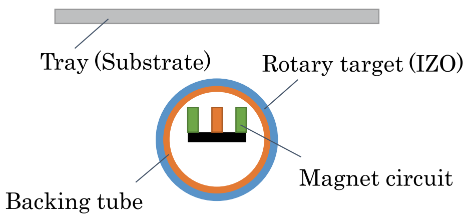

Fig. 5 Cross-section image of sputtering rotary cathode

3.4 OLED device evaluation

The configuration of the OLED device for which sputtering evaluation was performed is shown in Fig. 6. It is a top emission type device structure. Organic materials from HIL to EML were applied by spin-coating onto a substrate patterned with an anode electrode and allowed to dry. After that, the upper layers from the NaF to the Ag cathode electrode were formed by vapor deposition. The thickness of the Ag at this time was 18 nm. We formed the IZO as a cathode electrode and optical adjustment layer by sputtering, and then evaluated the effect of sputtering on the underlying film on the basis of device performance. The thickness of the IZO film was determined to be 67 nm, taking into account the light extraction efficiency due to the microcavity effect.

Table 2 shows the device evaluation results. For comparison, we fabricated devices by depositing IZO by means of a conventional sputtering process causing high damage and the low damage sputtering process Ver. 1, in which the cathode was modified to achieve low damage. We formed the reference device by vapor deposition of an organic film instead of IZO. The device characteristics evaluated were the drive voltage [V] when the current flowing per unit area to the OLED element was 10 mA/cm^2, and the current efficiency [cd/A] when luminance of 1000 cd/m^2

Fig. 6 OLED device configuration for sputtering process evaluation

Table 2 OLED device evaluation results for low damage sputtering process

	Reference Evaporation Process	Conventional Sputtering Process	Low Damage Sputtering Process Ver.1
Drive voltage @10mA/cm^2	100%	120.9%	104.7%
Efficiency @1000cd/m^2	100%	86.1%	94.4%

was obtained. In order to efficiently inject electrons from the cathode side where the IZO film is formed, current must flow at a low drive voltage, and it is preferable to obtain highly efficient light emission with a low current.

When the drive voltage and efficiency of the reference vapor-deposited OLED device are normalized to 100%, the conventional high-damage sputtering process shows a drive voltage increase of at least 20% and an efficiency decrease of at least 10%. Using the low damage sputtering process Ver. 1, however, we obtained a decrease of only about 5% in both the drive voltage and efficiency of the OLED device, suggesting that the damage was suppressed. The damage to the OLED device's underlying film caused by sputtering under high-damage conditions is thought to degrade its electron injection properties and increase the drive voltage. This degradation in its electron injection properties is also thought to be responsible for the decrease in efficiency.

3.5 Sputtering damage analysis and improvement to OLED

In order to further reduce damage, we attempted to quantify device performance and the damage factor caused by sputtering. We fabricated a probe for this evaluation and installed it at the substrate's location in order to acquire the state of the electrical discharge space during sputtering and analyze the damage factor by comparing the device's performance with that of devices fabricated under similar sputtering conditions. The device used for damage evaluation was based on the configuration shown in Fig. 6. We adjusted the configuration to make it more sensitive to damage, the details of which are omitted here.

The results of our analysis, shown in Fig. 7, indicate that the damage factor is strongly correlated with the drive voltage of an OLED device fabricated by sputtering. The straight dashed line is an approximation calculated from the points in this evaluation. The figure suggests that by reducing the damage factor, it would be possible to reduce the damage to the level occurring at a drive voltage equivalent to that of a vapor deposition device. As a proof of concept for a further low damage sputtering process, we improved the cathode and succeeded in creating the conditions of the target region shown in Fig. 7 (low-damage sputtering process Ver. 2).

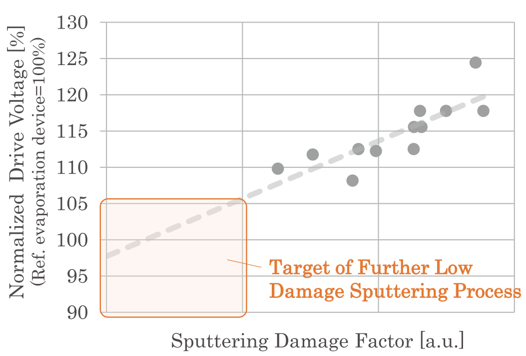

Fig. 7 Relationship between sputtering damage factor and drive voltage of OLED devices

Table 3 OLED device evaluation results for further damage reduction sputtering process

	Reference Evaporation Process	Low Damage Sputtering Process Ver.1	Low Damage Sputtering Process Ver.2
Drive voltage @10mA/cm^2	100%	98.2%	101.7%
Efficiency @1000cd/m^2	100%	92.4%	99.3%
Lifetime(T95) @25mA/cm^2	100%	86.4%	127.8%

Table 3 shows the evaluation results for the device associated with this further damage reduction sputtering process (Fig. 7). The results for low damage sputtering process Ver. 1 and the reference vapor deposition device are also shown for comparison. In addition to the drive voltage and efficiency, the lifetime of the device was also evaluated. To evaluate the lifetime, we set the initial luminance to 100% and measured the time for the luminance to decay by 5% at a fixed current density (25 mA/cm^2).

For the low damage sputtering process Ver. 1, the drive voltage was the same as that of the vapor deposition device, but the efficiency and lifetime were reduced by around 10%. However, for the newly developed low damage sputtering process Ver. 2, the drive voltage and efficiency were equivalent to those of the vapor deposition device, and the lifetime was equivalent to or greater than that of the vapor deposition device. We also measured the substrate temperature and confirmed that it was below 50°C, indicating that there was no significant increase in the substrate temperature.

Factors that may affect lifetime include material deterioration due to water or impurities, reduced carrier recombination probability due to interface defects, luminance degradation due to changes in carrier injectability, and defects caused by physical factors such as particles. It is not clear why devices fabricated by our sputtering process had a similar or longer lifetime than those fabricated by the vapor deposition process in this evaluation. In the future, it will be necessary to identify such lifetime deterioration factors by analyzing and isolating them.

(a) Condition with few particles generated during sputtering deposition

(b) Condition with many particles generated during sputtering deposition

Fig. 8 Observation of the lighting surface of OLEDs fabricated by our sputtering process

3.6 OLED device failure due to particles

As noted above, particles in OLED devices not only degrade device performance, but are also one of the factors that reduce product yield. We applied a forward voltage to the OLED device elements made by sputtering and observed the device surface when light was emitted (Fig. 8). Fig. 8(a) shows a device element with IZO deposited by the low damage sputtering process Ver. 1. Uniform light emission is seen on the surface, demonstrating that a normal device can be manufactured by using our sputtering process. Although not shown in the figure, we also confirmed that the low damage sputtering process Ver. 2 produced similar low-particle results. On the other hand, Fig. 8(b) shows a device element fabricated under conditions where particles are easily generated during IZO deposition. A large number of non-luminescent areas, called dark spots, were observed when light was emitted. Dark spots are thought to be caused by multiple factors[16). When the underlying organic film is exposed due to an abnormality in the cathode electrode section or a pinhole in the cathode electrode film, the organic film reacts with water or oxygen and loses its function as an OLED, causing a localized non-luminescent region. Dark spots are the starting point for the expansion of the non-luminescent region over time, which degrades the performance of the device.

Fig. 9 shows the J-V curves of the OLED device elements fabricated by our sputtering process. When a reverse voltage is applied to an OLED device in which many particles were generated at the time of IZO deposition, a high leakage current flows through the device, indicating that a flaw in the diode characteristics. Presumably this is because a short circuit is formed in the device element, triggered by anomalies like the aforementioned dark spots caused by particles.

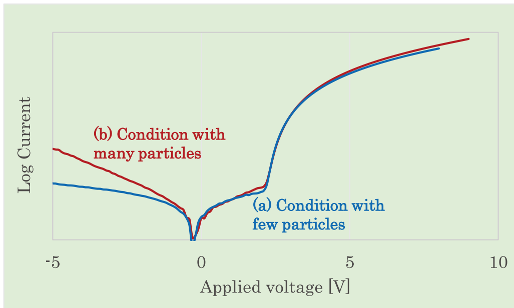

Fig. 9 J-V curve of OLEDs fabricated by sputtering process

With the OLED device configuration used in this evaluation (Fig. 6), despite the fact that IZO is deposited by sputtering on top of the pre-formed Ag cathode electrode, particles generated during film deposition cause the aforementioned dark spots and leakage currents. Although we lack a clear analysis at present, we believe that particle reduction will be an issue in the mass production of stable OLED devices. The sources of particle generation during sputtering include the target itself as well as the surrounding protective plates and structures. Since this varies depending on the sputtering conditions, it is necessary to pay at least as much attention to particle reduction as to the damage caused by sputtering.

4. Future issues and applications

In this paper, we evaluated sputtering damage by forming IZO on an Ag cathode electrode. However, in the future, in order to further expand the scope of applications for sputtering in OLED devices, we plan to replace the cathode electrode itself with a sputtering process. There are already some studies and reported cases of applications in top emission type device structures[17]. In addition, one of the main cost pressures on OLED versus LCD is the expensive organic materials. Researchers are working on ways to replace these organic materials in functional films with inexpensive inorganic materials, and have developed unique materials such as $C_{12}A_7$ electride[18] and ZSO[19], which have EIL and ETL functionality.

We believe that the challenge of replacing not only the cathode electrode but also the organic film conventionally formed by vapor deposition with sputtering has the potential to be a breakthrough technology that solves the cost and lifetime problems that have been bottlenecks in OLED devices. Going forward, we will continue to explore the possibilities of low damage sputtering processes for various devices and materials.

5. Summary

To improve light extraction efficiency, we evaluated a low damage sputtering process for OLED devices applicable to top emission type device structures and succeeded in obtaining device performance equivalent or better than the existing vapor deposition method. We also showed that for OLED devices, in addition to the damage caused by sputtering, which is a traditional concern, the suppression of particle generation will be an important issue in the future. Going forward, we will expand the range of applications for the sputtering process in OLED devices to further demonstrate the potential of OLEDs.

References

1) C. W. Tang and S. A. Vanslyke: Appl. Phys. Lett., 51, 913 (1987)
2) C. Adachi, S. Tokito, T. Tsutsui, and S. Saito: JJAP, 27, L269 (1988)
3) C. Hosokawa, H. Higashi, H. Nakamura, and T. Kusumoto: Appl. Phys. Lett., 67, 3853 (1995)
4) M. A. Baldo, S. Lamanky, P. E. Burrows, M. E. Thompson, and S. R. Forrest: Appl. Phys. Lett., 75, 4 (1999)
5) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi: Nature, 492, 234 (2012)
6) T. Furukawa, H. Nakanotani, M. Inoue, and C. Adachi: Sci. Rep., 5, 8429 (2015)
7) N. Takada, T. Tsutsui, and S. Saito: Appl. Phys. Lett., 63, 2032 (1993)
8) H. Kim, D.-G. Kim, K.-S. Lee, M.-S. Huh, S. H. Jeong, and K. I. Kim: Appl. Phys. Lett., 86, 183503 (2005)
9) H.-K. Kim, K.-S. Lee, and J. H. Kwon: Appl. Phys. Lett., 88, 012103 (2006)
10) H.-K. Kim, S.-W. Kim, K.-S. Lee, and K. H. Kim: Appl. Phys. Lett., 88, 083513 (2006)
11) T. H. Gil, C. May, S. Scholz, S. Franke, M. Toerker, H. Lanker, K. Leo, and S. Keller: Organic Electronics, 11, 322 (2010)
12) T. Welzel and K. Ellmer: J. Phys. D: Appl. Phys. 46, 315202 (2013)
13) Y. Hoshi, S. Kobayashi, T. Uchida, Y. Sawada, and H. Lei: J. Vac. Soc. Jpn., Vol. 59, No. 3 (2016)
14) K. Suemori, et al.: AIP Advances, 7, 045014 (2017)
15) M. Nagai: Journal of the Electrochemical Society, 154, J387 (2007)
16) Y. Fukuda: Hyomen Kagaku, Vol. 25, Issue 9. 594 (2004)
17) T. Kuroki, et al.: KONICA MINOLTA TECHNOLOGY REPORT VOL. 14 (2017)
18) H. Hosono, J. Kim, Y. Toda, T. Kamiya, and S. Watanabe: PNAS, Vol. 114, No. 2, 235 (2017)
19) N. Nakamura, J. Kim, and H. Hosono: Adv. Electron. Mater., 4, 1700352 (2018)

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