Present and trend of oxide phosphor thin film development for electroluminescent device applications

Toshihiro Miyata and Tadatsugu Minami
Optelectronic Device System R&D Center, Kanazawa Institute of Technology
7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501 JAPAN
Phone: 81-76-294-0714, E-mail: tmiyata@neptune.kanazawa-it.ac.jp
Keywords: electroluminescence, oxide phosphor, flexible, inorganic EL, see-through

Abstract

The present status and trend of oxide phosphor thin-film development for thin-film electroluminescent (TFEL) device application are presented in this paper. Recently, several newly developed types of bendable or bendable see-through oxide TFEL lamps have been fabricated using the TFEL technology with a newly developed bendable ceramic sheet, glass sheet or sapphire sheet substrate, which has become available on the market. Stable operation at high temperatures was obtained in double-insulating-layer-type TFEL lamps fabricated with a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin-film emitting layer forming on translucent or transparent bendable sheet substrates.

1. Introduction

Recent innovations in flat panel emissive displays and lamps have frequently required fabrication on a flexible substrate. For example, flexible organic light-emitting diodes fabricated on a flexible plastic sheet are being actively developed for flat panel display and lamp applications.[1-3] On the other hand, flexible hybrid-type-flat panel electroluminescent (EL) lamps that feature an emitting layer composed of a ZnS:Cu phosphor powder dispersed in an organic dielectric binder and printed on a flexible plastic sheet are already in practical use.[4] In addition, a new flexible hybrid-type EL device fabricated by combining sphere-supported oxide thin-film electroluminescent (TFEL) technology with a polypropylene-$BaTiO_3$ composite sheet has been recently reported.[5-7] However, high temperature operation is difficult to achieve for flexible flat panel light-emitting devices using flexible plastic substrates and/or organic materials. Recently, new flexible inorganic TFEL devices fabricated on bendable inorganic sheet substrates have been reported.[8-10] For example, new bendable oxide TFEL devices were fabricated on a bendable zirconia-based ceramic sheet.[8-10] In addition, bendable see-through oxide TFEL lamps were fabricated using the TFEL technology with a newly developed bendable glass sheet substrate.[10]

In this paper, present and trend of oxide phosphor thin film development for EL device applications are described. The description is focused on several newly developed types of bendable or bendable see-through oxide TFEL lamps fabricated using the TFEL technology with a newly developed bendable ceramic sheet, glass sheet or sapphire sheet substrate, which has become available on the market.

2. New Oxide TFEL Phosphor Developments

High-luminance oxide TFEL devices have been recently developed using a new combinatorial deposition technique featuring rf magnetron sputtering with a subdivided powder target.[11] As a result of successfully optimizing the chemical composition and/or the impurity content in various multicomponent compound phosphors, the improvement of EL characteristics in TFEL devices as well as the

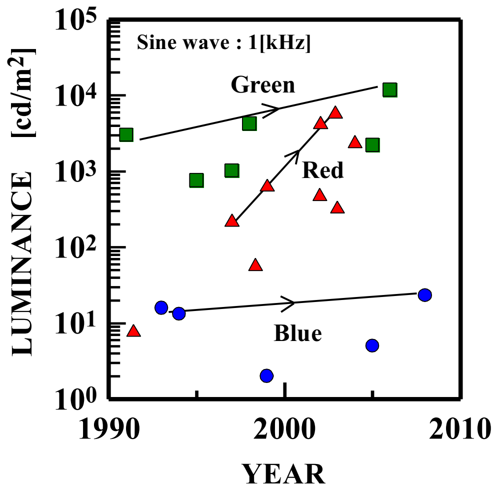


Fig. 1 The change of obtained maximum luminances in red-, green- or blue-emitting oxide TFEL device.

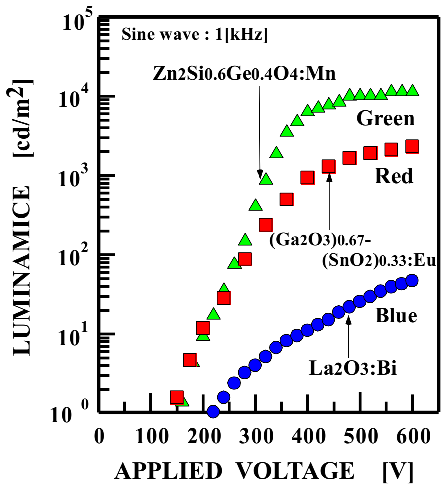


Fig. 2 Typical L-V characteristics for a red-, green- or blue-emitting TFEL device.

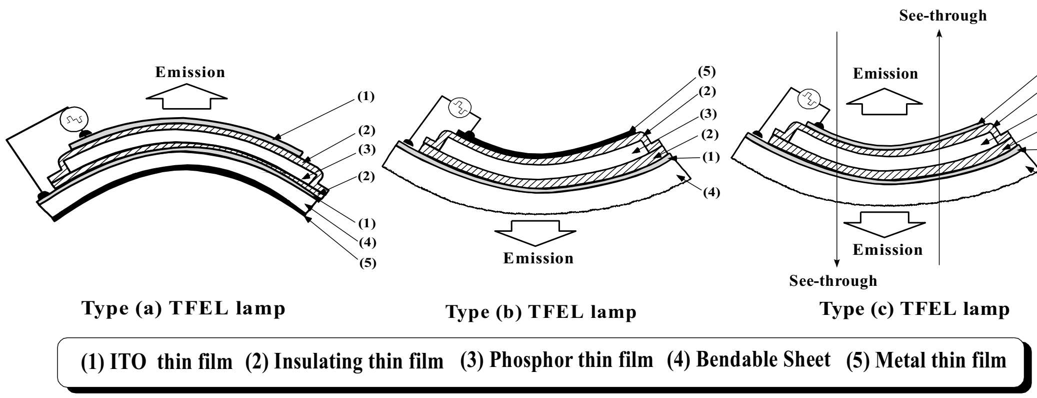


Fig. 3 Schematic diagrams of three types of bendable TFEL lamps.

development of new thin-film phosphors for TFEL applications have been reported. Figure 1 shows the change of the obtained maximum luminance in a red-, green- or blue-emitting oxide TFEL device fabricated using new phosphor materials, respectively. It should be noted that all the results were attained using a thick-ceramic-insulating-layer-type TFEL device structure. For example, the TFEL devices were fabricated by combining a phosphor thin-film emitting layer with a thick $BaTiO_3$ ceramic sheet (thickness of about 0.2 mm) insulating layer.[12] In the final TFEL device fabrication procedure, a transparent conducting Al-doped ZnO (AZO) thin film and an Al thin film back electrode were deposited on the phosphor thin-film emitting layer and on the $BaTiO_3$ ceramic sheet, respectively. As an example of utilizing the newly developed combinatorial deposition method, high luminances of 11800 and 1536 cd/m^2 in green emission were recently reported in TFEL devices fabricated using $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin films (Ge content of 40 at.%) with a Mn content of 2 at.% and driven at 1 kHz and 60 Hz, respectively.[1-3] In addition to green emission, a high-luminance blue emission was recently obtained in TFEL devices fabricated using newly developed La_2O_3:Bi phosphor thin films by utilizing the new combinatorial deposition method. A luminance of 48 cd/m^2 for blue emission was obtained in a TFEL device fabricated with a La_2O_3:Bi thin-film emitting layer with a Bi content of 2 at.% and driven at 1 kHz. Figure 2 shows typical luminance vs. applied voltage (L-V) characteristics for high-luminance red-, green- or blue-emitting oxide TFEL devices fabricated with a $((Ga_2O_3)_{0.67}$-$(SnO_2)_{0.33}$:Eu, $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn or La_2O_3:Bi phosphor thin-film emitting layer, respectively, and driven at 1 kHz. As can be seen in Fig. 2, red and green emissions from oxide TFEL devices are suitable for practical use in TFEL display and lamp applications. While, the obtainable luminance in blue emission was significantly increased by developing La_2O_3:Bi TFEL phosphors, however, it may be not yet satisfactory for practical use.

3. Flexible TFEL Devices

3.1 Device fabrication

Various bendable TFEL devices, some see-through, were fabricated by forming a conventional double-insulating-layer-type (D-type) device structure on three kinds of bendable substrates that have become commercially available in recent years : zirconia-based ceramic (Ceraflex A, Japan Fine Ceramics Co. Ltd.)[8], (OA-10 glass, Nippon Electric Glass Co. Ltd.)[10] and R-face sapphire (Kyocera Corporation) sheets with thicknesses of 50 or 100, 100 and 60 µm, respectively. As the first fabrication step, a transparent conducting indium-tin-oxide (ITO) thin film, functioning as a transparent electrode, was deposited on the sheet substrates at a temperature at 250^{o}C by dc magnetron sputtering (dc-MS) or r.f. magnetron sputtering (rf-MS).[8-10] For the fabrication of D-type TFEL devices, an amorphous multi-component oxide thin film was then formed by rf-MS as the first insulating layer on the ITO film transparent electrode. One of various phosphor thin-film emitting layers was next deposited by rf-MS on the first insulating layer of D-type devices. In order to improve the luminescent characteristics, the deposited phosphor thin films were postannealed at a temperature in the range from 500 to 910^{o}C in an Ar gas atmosphere for a duration of 10 to 60 min. After annealing, a nitride thin film and/or an oxide thin film were deposited as the second insulating layer, and then either an Al- or Ga-doped ZnO (AZO or GZO) thin film or an Al thin film was deposited as the top electrode by dc-MS, vacuum arc plasma evaporation (VAPE)[8-10] or vacuum evaporation, respectively. The EL characteristics of the resulting TFEL devices driven by an ac voltage were measured using a Sawyer-Tower circuit and a conventional luminance meter.

3. 2 Bendable TFEL lamps

Three types of bendable TFEL lamps were successfully fabricated by forming a D-type TFEL structure, as shown in Fig. 3, on a bendable translucent ceramic sheet, transparent glass sheet or transparent sapphire sheet substrate. Type (a) and type (b) TFEL lamps emit light through either the top transparent electrode or the bendable sheet substrate, while type (c) TFEL lamps emit light through both the top transparent electrode and the bendable sheet substrate. As a result, bendable TFEL lamps using the three types of device structures can provide different types of lighting. For example, type (a) and type (b) TFEL lamps were fabricated using translucent bendable ceramic sheet substrates; emission observable through the transparent top layer included direct emission from the phosphor thin film emitting layer as well as that reflected from the oxide ceramic sheet surface and emission observable through the back electrode passed directly through the translucent ceramic substrate. These type devices could produce a higher luminance than type (c) TFFL lamps. As an example of a bendable TFEL device incorporating a translucent bendable ceramic sheet, Fig. 4 shows L-V characteristic for a type (a) TFEL lamp fabricated using a postannealed $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film and driven by an ac sinusoidal wave voltage at 1 kHz. The device was fabricated by depositing a ITO, an amorphous multi-component oxide (mixture of BaO,Al_2O_3,Y_2O_3,TiO_2 and Ta_2O_5; or BAYTTO), a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn, a Si_3N_4 and a AZO thin film as the transparent electrode, the first insulating layer, the emitting layer, the second insulating layer and the top transparent electrode, respectively. The $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film was postannealed in an Ar gas atmosphere for 30 min at 910^{o}C. A high luminance of approximately 2010 cd/m^2 in

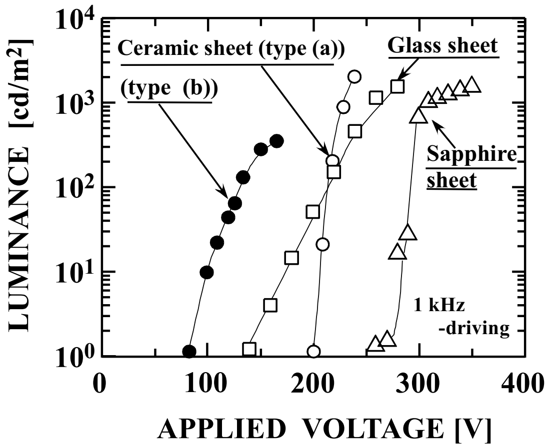


Fig. 4 L-V characteristics for $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamps formed on various bendable sheet substrates.

green emission was obtained in this type (a) TFEL lamp using a translucent bendable ceramic sheet substrate with the Al thin film deposited as the back reflector.

In addition to type (a), type (b) of bendable TFEL lamp was fabricated by forming a D-type TFEL structure, as shown in Fig. 3, on a bendable translucent ceramic sheet. As an example of a bendable type (b) TFEL lamp, Fig. 4 shows the L-V characteristic for a type (b) TFEL lamp fabricated using a postannealed $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film and driven by an ac pulsed voltage at 1 kHz. The device was fabricated by depositing a ITO, a BAYTTO, a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn, a Si_3N_4 and a Al thin film as the transparent electrode, the first insulating layer, the emitting layer, the second insulating layer and the back electrode, respectively. The $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film was postannealed in an Ar atmosphere for 30 min at 910°C. A high luminance of approximately 350 cd/m^2 for green emission was obtained in the $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamp. In addition, soft light emission that resulted from the light scattering effect in the zirconia-based ceramic sheet was obtained from the ITO side of the type (b) $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL device. It was found that both type (a) and (b) bendable $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn EL lamps, exhibited stable operation in air, even at a high temperature.

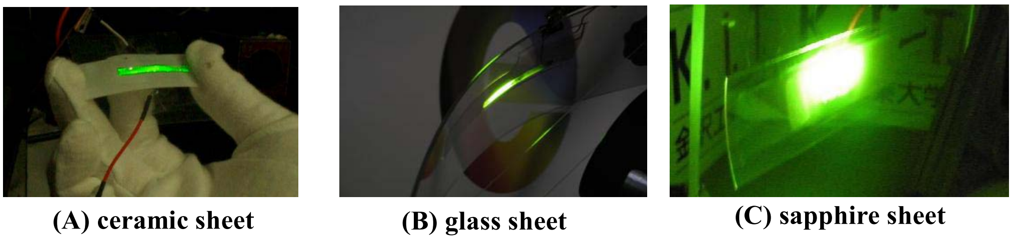
In addition, type (b) TFEL lamps were fabricated, using the same preparation conditions as described above, on a bendable transparent glass sheet or sapphire sheet substrate. In fabricating TFEL lamps with a bendable glass sheet, however, in practice, postannealing conditions are limited by the softening temperature of bendable glass substrates. As a result, suitable annealing conditions are strongly dependent on the device structure and the substrate material as well as the other materials used for the thin-film insulating and emitting layers. For example, it has been reported that a postannealing temperature above 650°C is necessary to improve the TFEL properties for $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL devices.[10] However, the use of a bendable glass sheet substrate in bendable TFEL devices presented here limited conventional heat treatments in various atmospheres to temperatures only up to approximately 600°C. Thus, we newly developed a rapid thermal annealing (RTA) process using an infrared (IR) lamp furnace because a conventional electric furnace proved to be difficult to use for the postannealing process. The RTA process was carried out in an Ar gas atmosphere. As a result, it was found that postannealing temperatures up to 910°C produced no observable deformation of the bendable glass sheets.

Type (b) TFEL lamps were fabricated on a bendable glass sheet or sapphire sheet substrate by depositing a ITO, a BAYTTO, a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn, a Si_3N_4 and an Al thin film as the transparent electrode, the first insulating layer, the emitting layer, the second insulating layer and the back electrode, respectively. The $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film deposited on a bendable glass sheet was postannealed in an Ar gas atmosphere for 1 min at 910°C by RTA. The $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film deposited on a bendable sapphire sheet was postannealed in an Ar atmosphere for 10 min at 910°C. The obtained L-V characteristics are shown in Fig. 4 for these TFEL lamps driven by an ac sinusoidal wave voltage at 1 kHz. As can be seen in Fig. 4, high luminances were obtained in both type (a) and (b) TFEL lamps, irrespective of the kind of sheet substrate used. Fig. 5 shows photographs of light emission from thin bendable TFEL lamps constructed using D-type TFEL devices fabricated with a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin-film emitting layer using translucent ceramic sheet or transparent bendable grass sheet or sapphire sheet.

3.3 Bendable see-through TFEL lamps

Bendable type (c) TFEL lamps fabricated on a bendable transparent sheet using transparent conducting oxide thin films as the front and back electrodes are see-through; TFEL lamps with a bendable translucent ceramic sheet were not see-through. However, type (c) TFEL lamps with a transparent bendable glass or sapphire sheet make possible bendable as well as see-through TFEL lamps. Figure 6 shows L-V characteristics of bendable see-through TFEL lamps fabricated with a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin-film emitting layer postannealed at 650°C and a transparent bendable glass sheet or R-plane sapphire sheet substrate. These devices are driven by an ac sinusoidal wave voltage at 1 kHz. In addition to high luminance from these bendable see-through $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL device, these devices exhibited stable operation in air even at a high temperature.

The resulting luminance as a function of operating



(A) ceramic sheet **(B) glass sheet** **(C) sapphire sheet**

Fig. 5 Photographs of light emission from the curved surface of $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamps formed on various substrates.

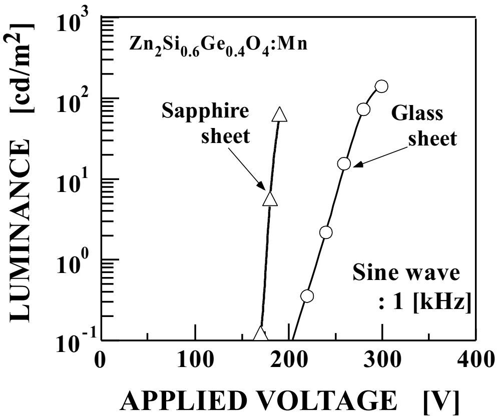


Fig. 6 L-V characteristics for bendable see-through $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamps.

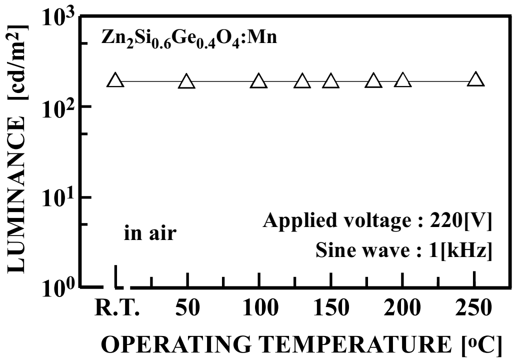


Fig. 7 Operating temperature dependence of obtained luminance from a bendable $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamp.

temperature is shown in Fig. 7 for a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL device driven by an applied voltage of 220 V at 1 kHz. This result demonstrates stable operation in air at temperatures up to 250^{o}C in a bendable see-through TFEL device fabricated using a $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn phosphor as the thin-film emitting layer. It should be noted that a high luminance in green emission was obtained in these bendable see-through TFEL lamps: emitting layer, $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn thin film; insulating layer, BaO, Al_2O_3, TiO_3 and Ta_2O_5 (BATTO) multi-component oxide thin film; transparent electrodes, ITO and GZO thin films; and substrate, bendable glass or R-plane sapphire sheet with a thickness of approximately 50 or 60 µm, respectively. As an example of bendable see-through $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamps, photographs of (A) and (B) in Fig. 8 show the TFEL lamp forming on sapphire sheet, without and with an applied 1 kHz ac voltage, respectively.

4. Conclusion

Thin and bendable inorganic thin-film electroluminescent (TFEL) lamps were fabricated by forming a double-insulating-layer-type TFEL device structure on three bendable sheet substrates. Three newly developed types of TFEL lamps that exhibited different light emission properties were demonstrated. High luminances in green emission was obtained in bendable TFEL lamps using $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn phosphor. In addition, see-through as well as thin and bendable inorganic TFEL lamps were fabricated by forming a double-

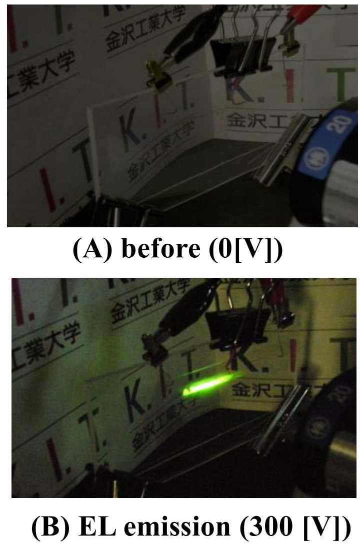


Fig. 8 Photographs of light emission from the curved surface of a see-through $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn TFEL lamp formed on a sapphire sheet.

insulating-layer-type oxide TFEL device structure on transparent bendable glass and sapphire sheets. High luminance in green emission was obtained in bendable see-through TFEL lamps using $Zn_2Si_{0.6}Ge_{0.4}O_4$:Mn phosphors. In addition, stable high- temperature operation was obtained in both bendable and bendable see-through TFEL lamps that used an oxide phosphor as the thin-film emitting layer.

Acknowledgments

The authors wish to acknowledge Prof. H. Fukada for fruitful discussion. And the authors also wish to acknowledge Mr. Y. Mochizuki, S. Matsui and K. Sahara for their technical assistance in the experiments.

References

1. M.Suzuki, T.Suzuki, T.Tsuzuki, S.Tokito, T.Kurita and F.Sato, *Proc. of the 11th Int. Display Workshops,* 1277 (2004).
2. T. Miyake, A.Yoshida, T.Yoshizawa, A. Sugimoto, H.Kubota, T.Miyadera, M.Tsuchida and H.Nakada, *Proc. of the 10th Int. Display Workshops,* 1289 (2003).
3. S. Logothetidis, Materials Science and Engineering, available online July (2008)
4. S.Shionoya and W.M.Yen, Phosphor Handbook, CRC Press, New York, (1999).
5. Y. Xiang, A.H. Kitai G. Quan, F. Zhang, Q. Liu and B. Cox: *SID '04 Digest of Tech. Papers*, 558 (2004).
6. A.H. Kitai, Y. Xiang, M. Bulk and B. Cox, *Proc. of the 12th Int. Display Workshops*, 1069 (2004).
7. Y. Xiang, A.H. Kitai and B. Cox: *SID '05 Digest of Tech. Papers*, 112 (2005).
8. T. Miyata, Y. Mochizuki, S. Tsukada and T. Minami, *Proc. of the 13th Int. Display Workshops*, 563 (2005).
9. T. Minami, and T.Miyata, *Proc. of the 6th Int. Meeting on Information Display/ The 5th Int. Display Manufacturing Conf.*, 27 (2006).
10. T. Miyata, H. Fukada, S.Matsui and T. Minami, *Proc. of the 15th Int. Display Workshops,* 929 (2007).
11 T. Minami, Y. Mochizuki, T. Miyata and K. Ihara, *Proc. of the 11th Int. Display Workshops*, 1135 (2004).
12 T. Minami, S. Orito, H. Nanto and S. Takata, *Proc. of 6th Int. Display Research Conf.*, 140 (1986).