

AC powder electroluminescent displays

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Abstract — The current status of AC powder electroluminescent (ACPEL) displays is reviewed with particular emphasis given to color and lifetime. The printing of the displays in forward and reverse architectures is also discussed, in addition to the fabrication of ACPEL displays with interdigitated electrodes, and different types of ACPEL phosphors and materials for back electrodes, transparent conducting electrodes, binders, and dielectrics are considered. Furthermore, shape conformable and highly flexible ACPEL displays are surveyed.

Keywords — AC electroluminescence, flexible displays, phosphors, electrodes, dielectrics, binders.

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1 Introduction

Following the pioneering work on AC powder electroluminescence (ACPEL) from zinc-sulphide-based material by G. Destriau in 1936,¹ reviews of work in the field were written in the 1960s by Henisch² and Ivey.³ Further reviews of more recent work were written by Pankove,⁴ up to 1980, and by Chadha,⁵ up to 1993. A chapter on AC powder electroluminescence (ACPEL) by Chen and Xiang appeared more recently in 2008⁶ and a review article on materials for ACPEL was published by Bredol and Dieckhoff in 2010.⁷

Electroluminescence is the emission of light by a material when it is subjected to an electric field. This sets electroluminescent phosphors apart from photoluminescent and cathodoluminescent phosphors, which emit light when excited by electron beams and electromagnetic radiation, respectively. There are two types of electroluminescence, namely, injection electroluminescence and high-field electroluminescence. The former occurs under relatively low fields and involves radiative electron-hole recombination at so-called p - n junctions. The latter occurs under relatively high fields and involves charge injection, again followed by radiative electron-hole recombination. It is high-field electroluminescence which is the subject of this paper.

It is worthwhile at this juncture to distinguish between the two fundamentally different types of AC electroluminescent devices that have been developed heretofore, namely, AC powder electroluminescent (ACPEL) devices and AC thin-film electroluminescent (ACTFEL) displays. Even though they are both classified as high-field electroluminescent devices, they are technologically very different because the former has a thick (typically on the order of tens of micrometers) emissive layer containing particles of phosphor powder, whereas the latter has a thin (typically on the order of tens of nanometers) emissive layer consisting of a crystalline phosphor film. Due to this difference in the

thicknesses of the devices, the powder phosphor of the ACPEL device is subjected to a much lower electric field (typically on the order of 10^4 V/cm) compared to that which is exerted on the thin-film phosphor (typically on the order of 10^6 V/cm). The difference in the magnitudes of the electric fields of the two types of devices causes the brightness-voltage curves to deviate in their characteristics with far reaching consequences for their display properties. In particular, the brightness-voltage curve of a thin-film ACPEL device shows threshold behavior when the phosphor layer experiences a Zener breakdown as electrons are injected by tunnelling into the phosphor layer.⁸ When this occurs, a small increase in voltage gives rise to a relatively large increase in brightness, unlike the brightness-voltage curve of an ACPEL device which shows a more gradual increase of brightness with voltage. The reasons for this divergence in the dependence of the brightness on voltage for the two types of devices are due to the underlying mechanisms responsible for generating the electroluminescence, which are beyond the scope of this review. However, the consequence is that the sharp non-linear brightness-voltage characteristic curve makes ACTFEL displays suitable for matrix addressing, whereas ACPEL displays have disadvantages when using this approach. This is because the off pixels of ACPEL devices can generate a background electroluminescence under the voltages that are applied to them in their “off” state, and this degrades the contrast ratio of the display.⁹ Nevertheless, passive-matrix-addressed ACPEL displays have been produced, although as far as we know they have not been commercialized.^{10–12} Matrix-addressed ACTFEL displays have been discussed previously¹³ and they are produced commercially by, for example, Planar.¹⁴ Furthermore, it should be mentioned that iFire Technology, Inc., developed 34-in.-HDTV prototype demonstrators based on ACTFEL technology and its proprietary thick dielectric,¹⁵ but it was unable to penetrate the market due to cost and performance considerations. No further atten-

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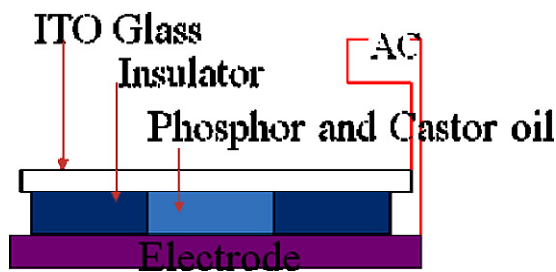


FIGURE 1 — A Destriau ACPEL cell consisting of a ZnS phosphor suspended in castor oil and sandwiched between two electrodes across which an AC voltage is applied.

tion will be paid to ACTFEL displays in this review, which will henceforth concentrate solely on the ACPEL technology.

Henry Joseph Round first observed the phenomenon of electroluminescence from silicon carbide, SiC, in 1907,¹⁶ and later reports of electroluminescence in silicon carbide by Lossev appeared in the 1920s.^{17,18} Gudden and Pohl studied photoluminescence from ZnS doped with copper, *i.e.*, ZnS:Cu, when subjected to an electric field in the late 1920s.^{19,20} They noticed that the effect of the electric field was to change the decay time of the photoluminescence, and this became known as the Gudden Pohl effect.

However, it is G. Destriau who is often credited with pioneering the field of powder AC electroluminescence from ZnS.¹ He applied an electric field to ZnS that is believed to have contained copper as an impurity. The ZnS was suspended in castor oil and this suspension was sandwiched between two electrodes, one of which was transparent, in a capacitor-like device (see Fig. 1). In Destriau's experiment the transparent conducting oxide (TCO) electrode consisted of a sheet of mica soaked in an electrolyte. This is a far cry from today's TCOs which usually comprise of indium tin oxide coated onto glass or polymer substrates for rigid and flexible devices, respectively. On applying an AC voltage across the electrodes, it was observed that green–blue light was emitted from the device through the transparent electrode. Although the Destriau cell is mainly only of historical interest, it is nevertheless useful in the laboratory as a quick and simple means of testing new ACPEL phosphor powders that are under development.

Although AC electroluminescence continued to be investigated by Destriau, among others, it was not until the 1950s that the first ACPEL devices were commercialized.

The first commercial ACPEL lamps were produced by GTE Sylvania in the 1950s; these consisted of phosphor and ceramic coatings fired on to steel plates. The uniform area light sources are well suited to certain applications such as exterior safety lights on aircraft and were first used on U.S. military jet fighters in the late 1960s. These days such lights are favored on many of the world's military aircraft, due to their ruggedness and capability of operating over wide temperature and altitude ranges.

Although the mechanism of AC powder electroluminescence has still not been fully elucidated, many investigations into the phenomenon have been carried out in order to advance our understanding. Notably, Fischer^{21,22} devel-

oped a model involving bipolar field emission into the zinc sulphide lattice from opposite ends of copper sulphide needles embedded within it. According to this model, after trapping of the injected holes at copper activator centres, and charge recombination with mobile electrons on field reversal, this gave rise to light emission in the form of lines or striations extending through most of the volume of the particles.

Although the Fischer model is still widely accepted, there have been few reports of the direct observation of the copper sulphide phase which is implicated in the field-emission process in the model. One of these is a short article by Ono *et al.*²³ reporting the detection of copper sulphide needles in the form of Cu₂S by means of XANES, another is a short report by Guo *et al.*²⁴ who observed a higher concentration of copper in the twin boundary areas and crystal streaks of sphalerite using high-resolution electron microscopy and scanning electron microanalysis, a third is a study by Y. T. Nien *et al.*²⁵ who reported the observation of ca. 50–80-nm Cu_xS precipitates from x-ray mapping of a transmission electron microscope, and a fourth is a recent article by Warkentin *et al.*²⁶ who maintained that copper sulphide is present in the form of tiny CuS-like clusters by means of EXAFS. However, others have found no evidence for copper sulphide needles,^{27,28} thus the precise nature of the role of copper sulphide clusters and the charge-generation process presently remain open to conjecture.

This article is by no means a comprehensive review of AC powder electroluminescence (ACPEL), rather it seeks to present some developments in the field over the last 15 years, drawing in particular from recent results in the authors' laboratories on ACPEL devices. The next section will discuss the materials aspects of ACPEL displays and this will be followed by a summary of the different types of ACPEL device, their architectures, and construction. This latter section will refer to some of the developments in the authors' laboratories, especially recent work on flexible ACPEL lamps and segmented ACPEL displays based on ink jet-printed metal electrodes. Finally, the future prospects of ACPEL devices will be assessed.

2 Materials for powder ACPEL displays

ACPEL devices can be regarded as light-emitting capacitors (LECs) in which an emissive layer is sandwiched between two electrodes, the front one being transparent for light out-coupling. The emissive layer consists of an ACPEL phosphor powder in a binder, and one or more optional layers of high dielectric material can also be inserted between the emissive layer and back electrode (*vide infra*). This section is divided into subsections on ACPEL phosphor powders, electrode materials, dielectrics, binders and color conversion materials.

2.1 ACPEL phosphors

2.1.1 Types of ACPEL phosphors

The most important material by far for ACCEL powder phosphors is zinc sulphide (ZnS). It exists in cubic (zinc blende) and hexagonal (wurtzite) polymorphs with the former being more stable at low temperatures (up to the phase transition temperature of ca. 1020°C).²⁹ In addition, a structural transition from hexagonal to cubic and a crystal growth with increasing copper doping (>400 ppm) has been reported for ZnS:Cu,Cl (1 wt.%) phosphor samples fired at 900–1050°C for 2 hours in a reduced atmosphere (3% H₂/Ar and sulfur).³⁰ The common activator in the ZnS lattice is the monovalent copper ion (Cu⁺) and this is normally accompanied by a charge compensation ion, such as a Cl[−] or Br[−] ion (Cl_S·Cu_{Zn}[′]) or a trivalent cation, such as Al³⁺ (Al_{Zn}·Cu_{Zn}[′]).^{31,32} The defect sites of these charge compensators are also believed to be shallow electron traps (donor levels). The ZnS:Cu,X (X = Cl, Br) phosphors emit blue–green light and the ZnS:Cu,Al phosphor emits green light when an AC voltage is applied across electrodes that sandwich the phosphor. The B–Cu emission band of ZnS:Cu,X (X = Cl, Br) phosphors increases in intensity relative to the G–Cu emission band as the frequency of the applied alternating voltage is increased (see Fig. 1).^{33–35}

The blue–green light emission can also be obtained when exciting the ZnS:Cu,X (X = Cl, Br, Al) with near UV light; for example, using the mercury emission line of wavelength equal to 365 nm.³⁶ This light emission has been attributed to electron–hole annihilation at copper recombination centers that are hole traps (acceptor levels), either copper ions substituting for zinc ions (Cu_{Zn}[′]), which have been reported to give rise to green emission (G–Cu), or proximal pairs of interstitial/substitutional copper ions (Cu_i·Cu_{Zn}[′]), which have been reported to give blue emission (B–Cu).^{36,37} An additional self-activated (SA) blue band, considered to result from electron–hole recombination at vacancies (V_{Zn}[″]), has also been suggested to contribute to the broad emission spectrum.^{38,39}

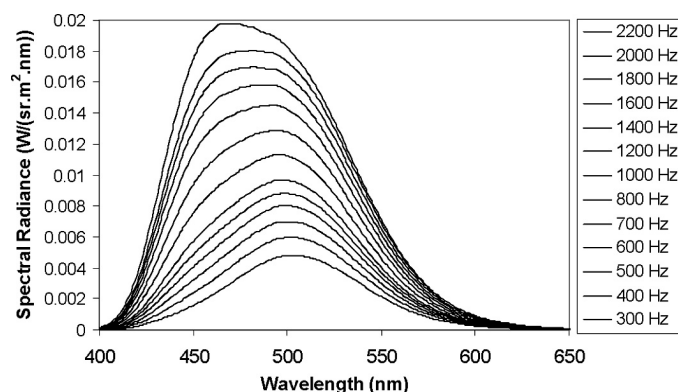


FIGURE 2 — Spectral radiance vs. wavelength of ZnS:Cu,Cl ACCEL phosphor under an applied voltage of 110-V RMS. The emission shows a shift from green to blue as the frequency is increased from 300 to 2200 Hz.

For a given frequency of the alternating voltage, green emission of ZnS:Cu,X (X = Cl, Br, Al) phosphor powders is favoured when the concentrations of the Cu activator and co-activators are nearly equal and blue emission is favored when the concentration of the former is higher than that of the latter.^{30,40} Furthermore, it has been reported that the blue–green emission can be shifted towards the blue by doping an alkali metal iodide, such as lithium iodide or potassium iodide, into the lattice.⁴¹ This apparently shifts the CIE *x,y* coordinates from *x* ≈ 0.180 to 0.184, *y* ≈ 0.424 to 0.426 for the phosphor without the alkali iodide dopant to *x* = 0.173 to 0.187, *y* = 0.392 to <0.424 with the alkali iodide dopant.

When a divalent manganese cation (Mn²⁺) is co-doped into the ZnS:Cu,Cl phosphor powder, a yellow emission (wavelength maximum equal to ca. 585 nm) is obtained under the influence of an AC field.^{5,42} This occurs due to energy transfer from Cu⁺ to the Mn²⁺ activator ions. The yellow emission has a maximum intensity at a wavelength that is close to the wavelength (555 nm) corresponding to the maximum of the photopic curve and it has been reported that, by controlling the levels of manganese, an efficient yellow-emitting ZnS:Mn,Cu,Cl phosphor can be made (>5.6 lm/W at 115 V/400 Hz).³⁴

In addition to the blue–green-emitting ZnS:Cu,X (X = Cl, Br), blue–green-emitting ZnS:Cu,Al and the yellow emitting ZnS:Mn,Cu,Cl phosphors that have previously been mentioned, other phosphors are based on (Zn,Cd) (S,Se,Te) lattices.⁴³ Ternary (Zn,Cd)S containing more than a few percent of CdS crystallize only in the hexagonal modification under normal preparation conditions, and the blue and green emission bands of hexagonal (Zn,Cd)S:Cu phosphors shift monotonically towards the red when zinc is gradually replaced by cadmium. At high Cd concentrations these emission bands shift into the infrared; the blue and green bands of hexagonal ZnS:Cu,Cl shift to 810 and 1080 nm, respectively, in CdS:Cu,Cl.⁴³ In contrast, it has been reported that the wavelength locations of the emission bands of Zn(S,Se):Cu and Zn(Se,Te):Cu phosphors depend relatively little on the S:Se or Se:Te ratios, respectively.⁴³ Other ACCEL powder phosphors that have been reported are (Zn,Mg)S:Cu,Br⁴⁴ and the silver activated (Zn,Cd)S:Ag,Cl⁵; both of these phosphors emit in the blue.

White ACCEL phosphor powders can be produced by mixing complementary blue-emitting ZnS:Cu,Cl and yellow-emitting ZnS:Mn,Cu,Cl phosphors.⁴⁵ An alternative possibility of using a single white-emitting ZnS:Mn,Cu,Cl phosphor, having Cu activated blue and green emission bands and a Mn activated yellow emission band, has also been investigated.⁴⁶ The color of ACCEL devices comprising the phosphor can apparently be altered from a warm white to a cold white by varying the relative concentrations of the Cu and Mn activators. However, it was noted that at high frequencies, the blue Cu-activated and yellow Mn-activated emission bands became saturated.⁴⁶

2.1.2 Synthesis of ACEL phosphors

The commonly adopted synthetic procedure for the preparation of ACEL ZnS:Cu,X ($X = \text{Cl, Br}$) phosphor powders involves a two stage firing, the first stage involving an annealing of a mixture of ZnS, copper salts, and fluxes at a temperature in the range of 1100–1400°C. This is followed by a mechanical treatment, such as ball milling, before the second stage firing is carried out at a lower temperature in the range of 500–1000°C.⁴⁷ Based on this general procedure, many patents have been granted for different approaches to the synthesis of these phosphors, as well as for ACEL device architecture.^{48,49} The synthesis of ACEL ZnS:Cu powders in terms of materials is relatively inexpensive, but the production is costly and complex.

A typical synthesis of some of our in-house ACEL ZnS:Cu,Cl phosphors uses the method reported by Take-mura,⁵⁰ which is described as follows. Osram-Sylvania ZnS (50 g) was stirred with an aqueous solution (50 cm³) of copper sulphate pentahydrate (0.15 g) for 0.5 hours. The slurried material was dried overnight at 150°C. 25 g of the dry material was thoroughly mixed with magnesium chloride (0.5 g), barium chloride (2 g), and sodium chloride (2.5 g). The mixed material was then fired at 1150°C for 4 hours.

The fired material was washed with hydrochloric acid, dried, and then pressed at a uniaxial pressure of 1.24 tons/cm² for 5 minutes. ZnO (5% by weight) was added and then the mixture was fired at 750°C for 1.5 hours. The fired material was washed again in hydrochloric acid, and after the pH had been adjusted, with KCN.

In addition, solution methods using thiourea dioxide and hydrazine hydrate have been developed in-house for the clean syntheses of ZnS based phosphors.^{51–55}

2.1.3 Encapsulating ACEL phosphors

The brightness of non-coated ACEL phosphors rapidly deteriorates due to the presence of moisture when an electric field is applied. Therefore, it is necessary to protect the phosphor particles from moisture by encapsulating them in a coating. There was an early report on the coating of ACEL phosphor particles as early as 1968,⁵⁶ but it was not until the early 1990s that they became available commercially, initially from the Durel Corporation. This was a big advance in the state of the art because it enabled the half-life of an ACEL lamp to be extended from approximately 500 hours to typically 3000 hours. In 2000, Durel and Osram Sylvania, who had been marketing EL, entered into litigation over the phosphor particle encapsulation process, upon which Durel had a patent. In late 2001, Osram and Durel came to a cross-licensing agreement assuring the future supply of EL phosphor. Although the brightness degradation is slower in encapsulated ACEL phosphors, it occurs nevertheless, and it has been shown by dynamic Monte Carlo simulations that the diffusion of copper species is a contributing factor.⁵⁷

Typically, inorganic coatings are applied for good moisture resistance. A preferred coating is aluminium oxy-hydroxide (AlOOH),^{58,59} although numerous other coatings have been applied, *e.g.*, titanium dioxide (TiO₂)⁶⁰ and aluminium nitride (AlN).⁶¹ The AlOOH coating can be applied to the ACEL phosphor particles by means of chemical-vapor deposition (CVD) using trimethylaluminium (TMA) and water-vapor precursors. The water vapor hydrolyzes the TMA to give an AlOOH coating on the surfaces of the phosphor particles, while the phosphor particles are suspended in a gas fluidized bed in order to ensure that the whole of the particle surface is exposed to the precursors to enable the particles to be coated conformally. Examples of such coatings are described in a number of U.S. patents.^{62–66}

The encapsulation of ACEL particles in AlN has the advantage that the particles do not need to be exposed to water or oxygen during the coating process. The AlN coatings can be formed from hexakis(dimethylamido)dialuminium, Al₂(N(CH₃)₂)₆, and anhydrous ammonia precursors, and luminous efficacies of 4–6 lm/W have been reported for AlN-coated ZnS:Cu ACEL phosphors.⁶¹

Currently, both oxide and nitride encapsulated powder phosphors are available on the open market. The CVD encapsulated ACEL phosphor particles always suffer a significant loss in initial brightness as a result of the coating process and it has been suggested that this may be caused by a decrease in the electric field inside the phosphor particles.⁵⁹ For example, the initial brightnesses of ACEL test lamps containing uncoated and AlOOH CVD-coated ZnS:Cu (Osram Sylvania Type 729) powder phosphors were reported to be 100.7 and 80.4 cd/m², respectively.⁵⁹ Atomic layer deposition (ALD) is apparently able to provide a thinner coating on the ACEL particles than the conventional CVD method while at the same time maintaining an equivalent level of moisture protection and at a higher level of initial brightness.⁵⁹ This is consistent with the initial brightness of 96.4 cd/m² that was reported for an AlOOH ALD-coated ZnS:Cu (Osram Sylvania Type 729) powder phosphor in an ACEL test lamp that was fabricated and driven under identical conditions to the above-mentioned test lamps containing uncoated and AlOOH CVD-coated ZnS:Cu powder phosphors.⁵⁹ The coating thickness of the AlOOH CVD-coated phosphor was measured to be 2000 Å by means of sputtered neutral mass spectrometry using a standard Ta₂O₅ film as a reference material, and this coating thickness value was in agreement with that estimated from the percentage aluminium content of the total coated phosphor weight that was measured by means of atomic-absorption spectroscopy. This coating thickness was approximately twice that of the ALD coated phosphor, which was measured to be 1160 Å, even though the CVD- and ALD-coated phosphors had nearly equal 100-hour maintenance in lamps. ALD is similar to CVD but the former uses pulses of the precursors in such a way that they are not present in the reactor in the vapor phase at the same time.^{67,68} This causes the precursors to react on the surfaces of the particles,

rather than in the gas phase, during ALD deposition. As the coating is formed essentially one layer at a time, denser coatings can be achieved than with CVD methods, albeit at a much slower deposition rate. It has been suggested that a more cost-effective method is a hybrid ALD/CVD process,⁵⁹ but this has not so far been realized on a large manufacturing scale.

2.1.4 Small-particle and nanoparticle ACEL phosphors

ZnS:Cu,X ACEL phosphors having an average particle size less than 25- μm have generally been undesirable due to inferior brightness and half-life characteristics. However, it has been claimed that a smaller-sized phosphor (having an average particle size of <ca. 23 μm) can be produced by manipulating the first stage firing temperature and time, and that the smaller phosphor particles have better half-life and brightness characteristics than those that can be obtained by sieving the standard phosphor.⁶⁹ Indeed, the smaller phosphor particles were reported to have a higher luminous efficacy than the standard particles due to their smaller size, but the disadvantage of this synthetic method is that it has a lower yield.⁶⁹ A later patent claims a method for making a ZnS:Cu-based ACEL phosphor having an average particle size less than 12 μm in diameter with reasonable brightness characteristics,⁷⁰ and two reports have appeared on the effects of particle size on the AC electroluminescence of ZnS phosphors.^{71,72}

Nanoparticles of ZnS:Cu,Al have also been observed to exhibit AC electroluminescence, emitting blue light when sulphur vacancies are present and green-light emission when they are absent.⁷³ Likewise, orange-light emission (590 nm) was observed when nanoparticles of ZnS:Cu,Al,Mn were used to form the emissive layer of an ACEL device. Interestingly, these ACEL devices had low turn-on voltages of ca. 10 V AC @100 Hz.⁷³ Nanorods of ZnS:Cu,Al, which were grown by self-assembly from solution, also exhibited AC electroluminescence at low voltages.⁷⁴ In addition, they showed other properties which were believed to be due to their self-assembly such as quenching of the lattice defect-related emissions accompanied by the enhancement of the dopant-related emission as well as super-linear voltage–brightness EL characteristics.

2.1.5 Electrode materials, dielectrics, and binders

It is usual to fabricate an ACEL device by screen printing each of the layers, *i.e.*, the front and back electrodes, the emissive layer, and one or more dielectric layers. A key enabler for ACEL devices was the development of transparent conducting SnO₂ films in 1950, triggering worldwide research and development of EL devices.⁷⁵ These days, indium tin oxide (ITO) sputtered films on polymer substrates, such as polyethylene terephthalate are commonly used. How-

ever, there is a major concern that the increased usage of indium is becoming unsustainable, and this is the impetus for considerable global research activity at the present time into searching for alternative transparent conducting oxide (TCO) materials. In particular, ZnO heavily doped with either Ga or Al, GZO, or AZO, is becoming a very attractive candidate for future generation TCOs.⁷⁶ Fluorine-doped tin oxide (FTO) is another alternative, but it has an average transmittance of only ca. 80% across the visible and its electrical conductivity is relatively low. Further possible alternative transparent conducting materials are 3,4-ethylenedioxythiophene, an organic polymer that is also known as PEDOT, and carbon nanotube (CNT) coatings. Since ITO is a brittle material, PEDOT is a useful alternative as a transparent conducting material for flexible devices, although its sheet resistance is 5–6 times higher than an ITO film with a sheet resistance of ca. 60 Ω/\square .⁷⁷ This was demonstrated when a film of ITO (100 nm thick) was measured to have a critical bending radius of 8 mm, beyond which its resistance increased intensely, whereas PEDOT (100 nm thick) remained stable. Furthermore, resistance measurements of PEDOT showed no significant change after >30,000 bending cycles at a radius of 8 mm.⁷⁷

The most widely used inks for the back electrode of ACEL devices are silver and carbon-loaded inks. Silver inks can routinely achieve conductivities of <1 Ω/\square (at ca. 10- μm thickness). Carbon-loaded inks are significantly cheaper, but their conductivity is usually 1–2 orders of magnitude worse than that of silver. Hence, they are best suited for smaller-area ACEL devices where electrical conductivity is less of an issue.

The dielectric layer usually consists of barium titanate ferroelectric, which is screen printed as a paste containing the BaTiO₃, with a polymer binder and plasticizer, and there are several such pastes available commercially. A different approach has been suggested recently; namely, the use of a BaTiO₃ ceramic sheet, prepared by a “peel-off” process, instead of the conventional screen-printed dielectric.⁷⁸ A slurry paste of a mixture of BaTiO₃, toluene/ethanol solvent system, an ester surfactant as a dispersant, polyvinyl butyral (PVB) as a binder, and dioctylphthalate as a plasticizer was printed on a polypropylene film, and it was then dried at 80°C to form a green sheet. The green sheet was then fired at 1250°C on a zirconia-coated alumina substrate to give a ceramic sheet having a thickness of ca. 50 μm . An emissive layer of ZnS:Cu,Cl phosphor powder in an organic binder was then printed on top of the ceramic sheet and then a transparent conducting ITO electrode was formed on top of the emissive layer. Finally, the ceramic sheet was peeled off the alumina substrate and a metal electrode was printed on to the exposed side of the ceramic sheet. These ceramic sheets apparently had a high dielectric constant of over $\epsilon_r = 8800$,⁷⁸ and the luminance of the ACEL devices prepared with the ceramic sheets (1073 cd/m² at a drive voltage of 200 V and a frequency of 1 kHz) was over three times that of conventional devices prepared with a dielectric paste.⁷⁸

This surprisingly high value of the dielectric constant of barium titanate approaches values of up to 10,000 that can be achieved at the Curie temperature of ca. 400K, and it is noteworthy that these values of the dielectric constant are considerably higher than the values of 2000–3000 that are obtained at room temperature.⁷

Various binder materials have been suggested for the emissive and dielectric layers. One possible material is “Cyano-resin,” supplied by Shin-Etsu. This is a solvent-borne cyano-derivatized cellulosic material, with a very high dielectric constant of ca. 18, and is thus capable of producing very bright lamps. Its drawbacks are that it is expensive, comparatively brittle and has a high affinity for water. Polyvinylidene fluoride (PVDF) is another possible binder material⁷⁹; unfortunately, it tends to be resistant to most solvents, but N-methylpyrrolidone or dimethyl sulphoxide can be used to dissolve it, notwithstanding the health and safety issues that need to be addressed.

It is noteworthy here to mention that the authors have carried out extensive investigations over the last decade on devices that do not have separate dielectric layers⁸⁰. The advantages of using a single, combined emissive/dielectric layer are that this approach enables more flexible ACEL displays to be fabricated and savings can be made both in materials and the number of printing steps. In order to enhance the dielectric properties of the single layer, the binder is loaded with nanoparticle BaTiO₃ ferroelectric as well as the ACEL phosphor powder. There is, however, a practical limit to the amount of inorganic material that can be added to the resin before the dried, printed layer starts to become embrittled and porous. Thus, the addition of dielectric powder reduces the amount of phosphor that can be incorporated, and a fine balance needs to be achieved to maximise emission.

2.1.6 Color-conversion materials

Although red ACEL phosphors have been reported,⁸¹ they are not sufficiently efficient for practical application. Consequently, color-conversion materials (CCMs) are usually used to generate a red-color in ACEL displays by wavelength conversion of the blue–green ACEL emission. Rhodamine dyes are far and away the most commonly used CCMs for this purpose, normally by incorporating them into the phosphor binder. Although rhodamine dyes are very efficient as CCMs, this approach does have its drawbacks. For example, the dyes tend to be degraded by sunlight and they impart a garish pink coloration to the lamps (when not energized) which may not be acceptable in some applications. Alternatively, inorganic phosphors may be used as CCMs for ACEL displays such as the red phosphors used as CCMs for blue LEDs, *e.g.*, CaS:Eu²⁺ or SrS:Eu²⁺.⁸²

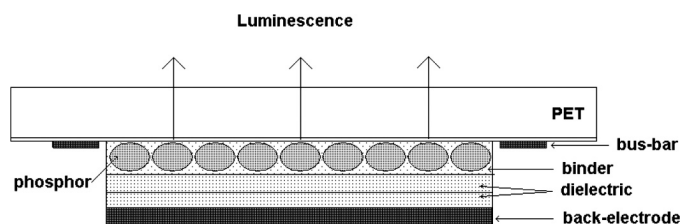


FIGURE 3 — Conventional forward architecture ACEL device.

3 ACEL display devices

The basic concept is that an ACEL lamp is essentially a lossy capacitor in which the AC electroluminescent phosphor particles need to be insulated from the electrodes of the ACEL cell in order to avoid short circuiting of the device. This can be achieved using a number of different architectures, as follows.

3.1 Architectures

3.1.1 Conventional forward architecture

Figure 3 illustrates the architecture of a conventional ACEL. The front (transparent) electrode consists of a sputtered layer of indium tin oxide, typically 40–120 Ω/□, on a glass or polymer substrate. The higher conductivity material is more expensive and has slightly inferior transmission properties and so it is perhaps best used for larger panels. To prevent power losses in the low-conductivity ITO coating it is normal to print a bus-bar around the periphery of the device (in the same print operation that applies the back electrode).

The phosphor layer is normally printed directly onto this substrate, followed by one or more layers of dielectric. The dielectric layers serve two purposes: firstly, to provide additional electrical isolation to prevent shorts between the electrodes. The second purpose is to act as a reflector.

As previously mentioned, with judicious formulation it is possible to achieve sufficient electrical isolation using the binder alone, without additional dielectric layers. This reduces the costs of manufacture substantially, albeit at the expense of a slight loss in performance. Another advantage of this approach is that by using a transparent conductor for the back electrode it is possible to produce double-sided lamps that emit in both directions.

3.1.2 Reverse architecture

Figure 4 illustrates a reverse architecture ACEL lamp. This type of ACEL device can be printed onto any solid surface. All of the various layers mentioned above are printed in reverse order. The primary difference is that the transparent front electrode is always printed in this case.

The great advantage of this architecture is that it can be applied to any substrate, provided it is compatible with the inks in terms of being solvent resistant and being able to withstand the drying temperatures.

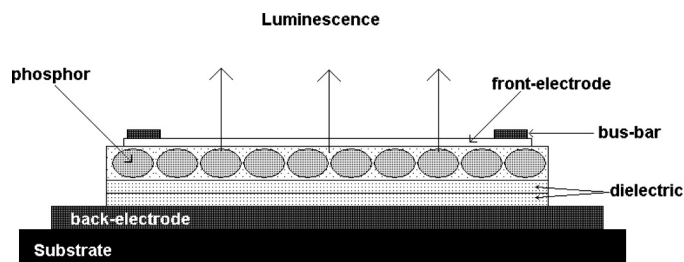


FIGURE 4 — Reverse architecture ACEL device.

Generally, the optical-transmission and electrical-conductivity properties of printed transparent electrodes are not quite as good as those of sputtered ITO, and therefore the lamps tend to be slightly less bright. This approach can be significantly cheaper, however.⁸³

3.1.3 Floating electrode architecture

An alternative architecture has been designed using two driven electrodes made from high-conductivity materials and a third, floating, electrode made from a transparent electrode material, as in Fig. 5.⁸⁴ In this configuration, the device essentially behaves like two ACEL cells in series. The drawback with this approach is that the voltage across each of the two ACEL cells is one-half of the applied voltage and thus, in order to achieve a brightness equivalent to that of a conventional ACEL lamp, twice the voltage must be applied which may not be acceptable in some circumstances. Additionally, the gap between the electrodes does not illuminate which may not be acceptable.

If the two halves of the structure are not identical in area, then the smaller ACEL cell will have a lower capacitance. As a result, more of the applied voltage will be dropped across it, and so it will be brighter than the larger ACEL cell. It is possible to use this property to make two-tone ACEL displays.

3.1.4 Interdigitated electrode architecture

An alternative way of producing ACEL lamps that requires no transparent electrode is shown in Fig. 6.^{85–88} In this architecture, interdigitated electrodes are printed in a single print run, for example, by offset lithographic printing,⁷⁵ and a phosphor layer is printed on top of them. The lateral field

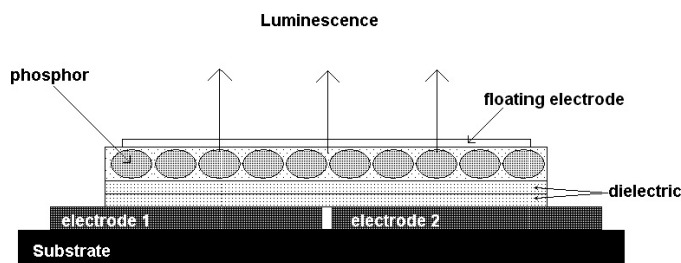


FIGURE 5 — Three-electrode ACEL device (reverse architecture).

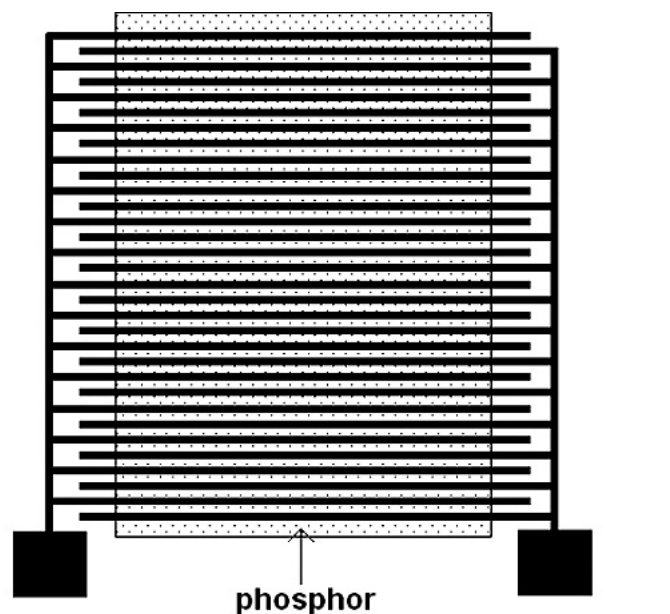


FIGURE 6 — Interdigitated electrode ACEL structure.

between the electrodes energizes the phosphor, and so it is necessary to keep the electrode gaps narrow, and certainly no more than 200–100 μm .

The advantages of this structure are clear: it only requires two print runs to form the device and it can be printed onto any substrate. Unfortunately, there are also substantial drawbacks with this approach that have meant that it has not been widely adopted. Typically, it is more than an order of magnitude less bright than conventional devices. For example, for an electrode track spacing of 100 μm , a brightness of 12 cd/m^2 was measured at a drive voltage of 250 V and a frequency of 1000 Hz.⁸⁹ Similarly, a brightness of 24 cd/m^2 was measured under the same conditions except for a drive frequency of 5000 Hz.⁸⁹ In part, these low values result from the practical difficulty of printing the electrodes close enough together using conventional print technologies. Additionally, the phosphor only emits light in the gaps between the electrodes, but not immediately above them. Thus, the interdigitated structure is clearly evident in the pattern of emission.

If printed onto a transparent sheet, then the device can be viewed from both directions, although it will be brighter from the phosphor side.

3.2 Flexible ACPEL displays

There is currently much interest in flexible, paper-like displays for information storage and presentation, and we have previously reported several aspects of our work on flexible EL powder displays.^{80,90,91} The aims of the work in our program were:

- (a) To develop a low-cost, paper-like display based on using powder AC electroluminescence (ACPEL)

that would be usable for short periods of time such as days or weeks.⁸⁰

- (b) To develop highly flexible lamps that can be bent around pre-formers.
- (c) To develop ACPEL lamps to be capable of repeated flexing, for example, in keyboards for mobile telephones.

The objective was to develop ACPEL displays that are based on paper or polymer substrates using a variety of electrodes such as deposited metal films, ITO (on polymer), or printed conducting layers.^{85,91}

3.2.1 Flexible ACPEL displays in the forward architecture

These displays are very simple and consist of a binder layer that is fabricated to lie between two electrodes.^{85,91–94} The single binder layer used in this work acts as a vehicle for carrying both the ACEL powder and the BaTiO₃ ferroelectric material, as discussed in Sec. 3.1.1.

To optimize such displays, it is useful to understand their microstructure, as will be discussed below (studied by SEM). Both the microstructure of the various layers and properties of some of the EL display layers will be com-

pared to those of conventional EL display layers that are thicker and less flexible.⁹⁰

Figures 7 and 8 show typical SEM micrographs of the very flexible ACEL layers, whereas Figs. 9 and 10 show SEM micrographs of more-conventional multilayer ACEL devices. In the SEM in Fig. 7(a), the structure of a new very flexible ACEL layer removed from the substrate and cut in thin section is presented. The inner layer is the binder containing the electroluminescent phosphor particles (up to 30 μm in size) surrounded by the much smaller ferroelectric micrometer particles (1–3 μm).

The outer layer is the covering electrode consisting of silver flakes embedded in resin. This layer is less flexible than the binder layer as can be seen where it has split at the top of Fig. 7 [see Fig. 7(a)]. The joint layer thickness is around 38 μm . A close up of the layer structure is seen in Fig. 7(b). It is apparent in Fig. 7(b) that in the binder layer each ZnS phosphor particle (large particles around 20 μm or more in size) is totally surrounded by the smaller 1–3- μm ferroelectric particles.

In Fig. 8(a), an SEM is shown of a new very flexible ACEL layer that has become detached from its PET substrate [seen in the top left hand corner of Fig. 8(a)] by the fixing material used to mount the sample for SEM studies penetrating behind the binder layer cut in thin section. The

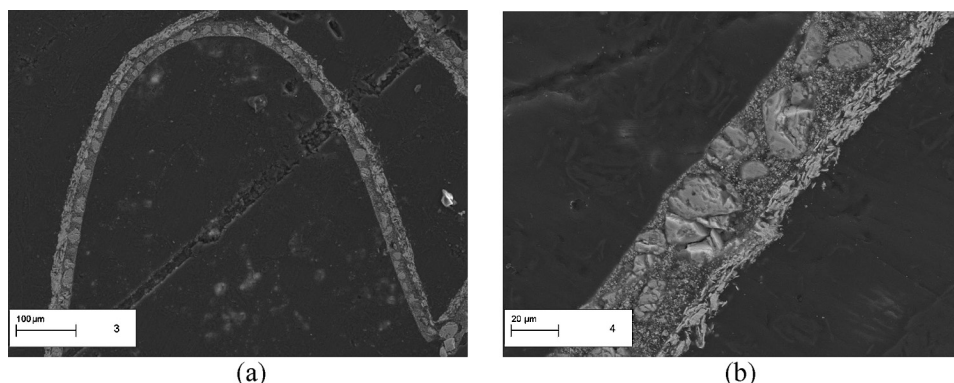


FIGURE 7 — (a) SEM of a new very flexible ACEL layer removed from the substrate and cut in thin section and (b) SEM close up of the same layer of a new very flexible ACEL layer shown in (a).

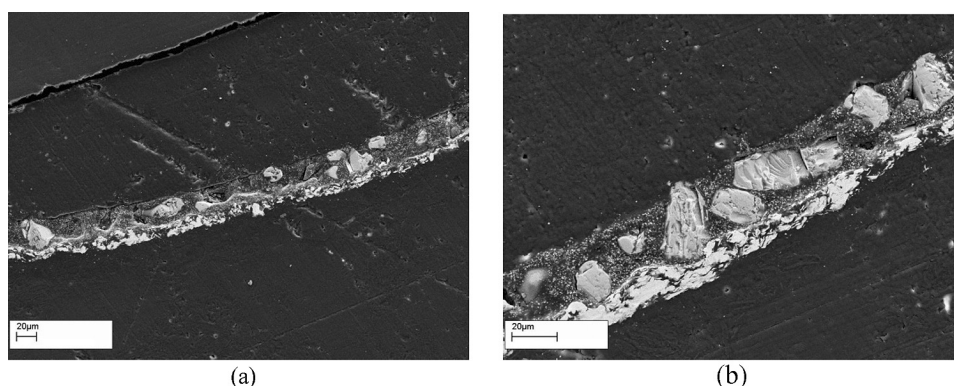


FIGURE 8 — (a) SEM of a new very flexible ACEL device detached from its substrate (seen in the top left-hand corner) and cut in thin section. (b) SEM of close up of the same layers of a new very flexible ACEL device shown in (a).

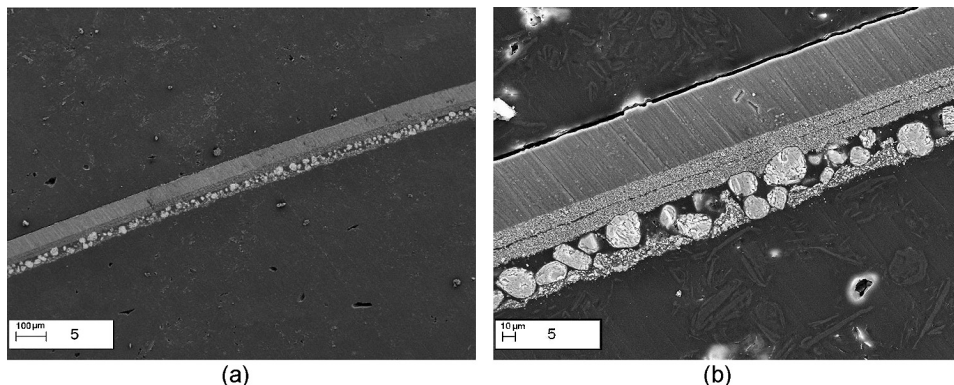


FIGURE 9 — (a) SEM of a conventional multilayer flexible ACEL device on an aluminium substrate (cut in thin section). (b) SEM (of a close up) of the conventional multilayer flexible ACEL device shown in (a).

inner layer is the binder containing the ACEL phosphor particles (up to 30 μm in size) surrounded by the much smaller ferroelectric particles. The outer layer is the covering electrode consisting of indium tin oxide particles embedded in resin. The joint layer thickness is ca. 40 μm . A close up of the layer structure is seen in Fig. 8(b). The PET substrate seen in Fig. 8(a) is covered by a thin ITO conducting layer that is too thin to see at this magnification.

Figure 9(a) shows a SEM of a conventional multilayer flexible ACEL layer on an aluminum substrate cut in thin section. In front of the substrate, two conventional layers of dielectric-containing ferroelectric micrometer particles can be seen, covered by a layer containing the electroluminescent phosphor particles (up to 30 μm in size); finally, there is the top electrode of ITO particles in a resin. The combined dielectric and top layers are over 60 μm thick. A close up of this layer structure is shown in Fig. 9(b).

Clearly, the new flexible binder layers shown in Figs. 7 and 8 are thinner than that in Fig. 9. Also in Fig. 9(b), it is apparent from the dark line separating them that the two dielectric layers are not well joined to each other and this can be a problem causing poor performance. This is not a problem for the new structure which eliminates the need for these dielectric layers.

The new binder layer (as presented in Figs. 7 and 8) in the new very flexible ACEL displays can withstand voltages of up to 300 V without failing.

Figure 10(a) shows a SEM of a conventional multilayer and flexible ACEL layer on an ITO-coated PET substrate cut in thin section. The substrate is covered by two dielectric layers containing ferroelectric micrometer particles, covered by a layer containing the ACEL phosphor particles (up to 30 μm in size), and finally there is the top electrode of ITO particles in a resin. The combined dielectric and top layers are over 80 μm thick. A close up of this layer structure is shown in Fig. 10(b). In Fig. 10(b), the boundary between the two dielectric layers is again apparent.

It should be noted that the new flexible binder layer only needs one pass through the screen printer, whereas the conventional structure needs at least two dielectric layers and the layer containing the electroluminescent phosphor particles, and therefore requires at least three passes through the screen printer.

So, from this discussion of novel structure for flexible EL displays compared to conventional structures, it has been shown herein that

1. The single layer devices are both cheaper in materials used and also in labor costs as they only require a single pass on a screen printer.

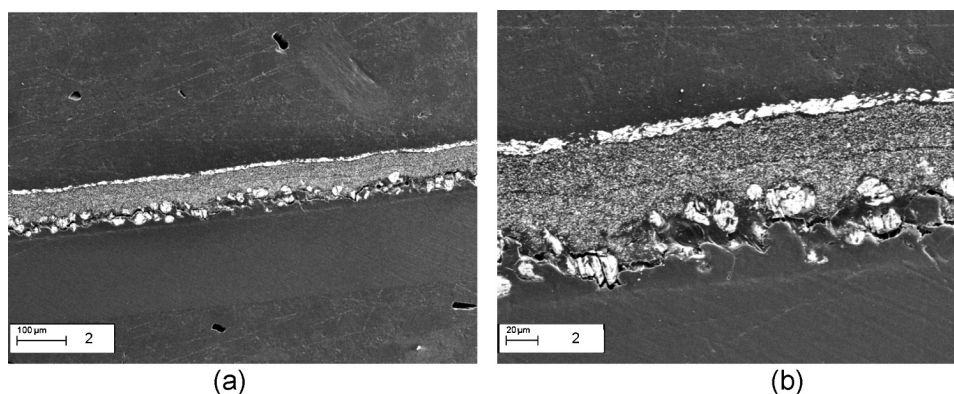


FIGURE 10 — (a) SEM of a conventional multilayer flexible ACEL layer on an ITO-coated PET substrate cut in thin section. The PET substrate is under the ACEL phosphor particles which are in a commercial resin. (b) SEM close up view of the conventional multilayer flexible ACEL layer shown in (a).

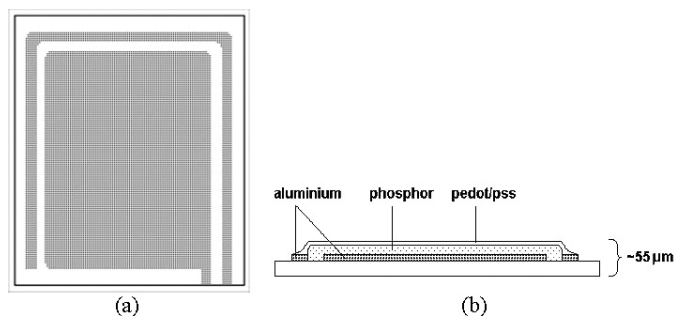


FIGURE 11 — (a) Pattern metallized PET and (b) schematic cross section of a typical device structure.

2. The single-layer architecture allows much brighter devices to be constructed, as it has enabled brightnesses of ca. 200 cd/m² to be achieved when driving at an AC voltage of 110 V and a frequency of 400 Hz.⁸⁰

The microstructure of the layers making up the displays has also been compared to more conventional structures and has been shown to be superior in a number of ways, such as flexibility and thickness as well as ease of construction.

3.2.2 Flexible ACEL displays in the reverse architecture

One of the main drawbacks on making highly flexible ACEL displays is that conventional ITO on PET is not very flexible. To avoid the restricted flexibility associated with ITO, a reverse architecture was used,⁸⁰ with the luminescence being transmitted through a transparent printed front electrode rather than through a transparent conductive oxide electrode that has been sputtered onto a substrate such as PET.

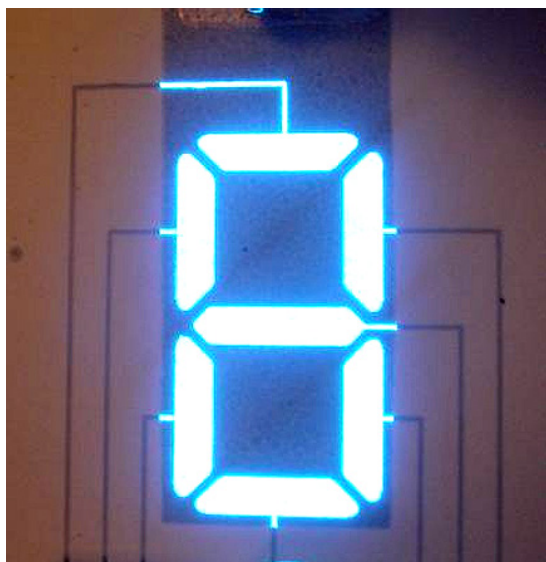


FIGURE 12 — An ACEL alphanumeric printed on a flexible substrate using a combination of ink-jet printing (for the segmented silver back electrodes) and screen printing (for the emissive layer and transparent top electrode).

To improve flexibility, a 23-μm-thick PET film was used as the substrate. To facilitate screen printing, the sheet was held by vacuum against a microporous sheet. The sheet was coated with an evaporated layer of aluminium. Aluminium adheres strongly to PET and is both highly conductive and highly reflective. For example, a coating of only ca. 25 nm in thickness typically has a resistance of only 1.1 Ω/□ and a light transmission of ~0.1%.⁹⁵ This is similar to the conductivity of a screen-printed silver coating of ca. 10 μm thickness.

Metallized polyester of this type is used in a wide variety of applications, such as food packing. As a result, it is produced in bulk quantities and is a low-cost material. The aluminium has mirror-like reflectivity, substantially better than silver inks, which helps to reflect luminescence back towards the viewer. This is particularly important in this case where, to enhance flexibility and reduce costs, no dielectric layer was used.

The metallized substrate material can be used directly, but it is most conveniently used after patterning. Figures 11(a) and 11(b) illustrate the architecture of a typical device, with a bus-bar.

In recent work, the authors have investigated the use of ink-jet printing to deposit the back electrodes in reverse-architecture devices, thereby enabling a range of flexible substrates to be employed, including Ref. 83. Indeed, when specially coated paper substrates are used, we have found that we can achieve a large increase in the intensity of the AC electroluminescence due to the mirror-like reflectivity of the ink-jet-printed silver.

The ink-jet-printed back electrodes in such reverse architecture ACEL lamps can be easily and quickly patterned by ink-jet-printing metal containing inks (*e.g.*, silver and copper), as is exemplified by the alphanumeric ACEL lamp shown in Fig. 12.

Moreover, the fact that ink-jet printing enables the back electrode to be patterned with high resolution has provided the capability to print twotone ACEL images, *e.g.*, for logos and emblems (see Fig. 13).



FIGURE 13 — A flexible printed light-emitting display based on a patterned electrode architecture, whereby shading effects are obtained by varying the spacings of the electrode pixels using CAD designs and ink-jet printing.

4 Conclusions

ACPEL phosphor powders and devices have been discussed. It is clear that there are a limited number of types of ACPEL phosphor powder at the present time and most of these are based on ZnS lattices. Moreover, the emission colors are also restricted to blue, green, yellow, and white.

The attraction of AC powder electroluminescence is due to the low cost of the technology, the fact that the lamps can be easily screen printed and that they are robust and not very sensitive to moisture or oxygen. In addition, flexible ACPEL displays are of considerable current interest due to their potential for being used as paper-like displays.

Where the application involves the flexible ACPEL display being subjected to bend cycles, the conventional ITO transparent conducting electrode material is unsuitable due to its friable nature. However, we have shown that the use of this material can be obviated by employing an interdigitated electrode structure that may be deposited onto numerous types of flexible substrates using offset lithographic printing of, for example, silver inks. Some possible applications for such displays include signage, backlights, toys, greetings cards, and other niche products.

Another alternative transparent conducting material to ITO for flexible ACPEL displays is the organic polymer 3,4-ethylenedioxythiophene, which is also known as PEDOT. ACPEL displays are already being produced on some items of clothing such as T-shirts and jackets as items of fashion or for safety applications. However, there is plenty of scope for extending the use of ACPEL displays in the field of wearable electronics, and flexible displays are an enabling technology for such applications.

Our recent application of ink-jet printing for the deposition of the back electrodes has demonstrated high-resolution images can be achieved by this method. Indeed, ink-jet printing can also be used to control the amount of electrode material present as well as its precise location on the surface of the substrate. Therefore, it is possible to build not only a segment of the display but one that is only partially covered by the electrode material. Such high-resolution images are well-suited for displaying logos and simple alphanumeric information for advertising applications, and their impact can be enhanced when the ACPEL display is animated in order to catch the eye of the onlooker. It is anticipated that these kinds of ACPEL displays, which are enabled by ink-jet printing the back electrodes, will find wider usage for advertising products at the point of sale in the retail industry and as logos or emblems on clothing and packaging. Such displays can also be designed to peel-off substrates, which can even be biodegradable or bio-soluble, in the interests of producing eco-friendly displays for a more sustainable future.

Finally, it should be emphasized that light-emitting components based on ACPEL technology can be readily and rapidly designed using CAD software, and produced by means of a combination of ink-jet and screen printing without the need to rigorously eliminate atmospheric oxygen and moisture. Indeed, ACPEL technology exemplifies some

of the advantages of the increasingly popular field of printed electronics that can be achieved, such as additive printing and design flexibility.

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