



**A MULTI-LAYER COMPOSITE FILM AND A METHOD FOR FORMING A  
MULTI-LAYER COMPOSITE FILM**

**Field of the invention**

5 The present invention relates to a multi-layer composite film and a method for forming a multi-layer composite film as a barrier substrate for flexible electronics devices and displays, such as organic light emitting device (OLED) displays, liquid crystal device displays (LCDs), and plastic electronic devices with displays, for example electronic cards, smart cards and the like.

10 **Background of the invention**

The development of flexible electronics devices and displays such as organic light emitting device displays (OLEDs), liquid crystal device displays (LCDs) and plastic electronic devices with displays depends largely on the achievement of a superior barrier substrate material. Polymer films are potential suitable  
15 substrate materials for such applications except for their poor barrier performance against, for example, moisture and oxygen. When used, for example, in display devices, there is a further requirement for the substrate material to have a high optical transparency, such as more than 85% optical transmission.

20 To improve the barrier properties in such devices, ultra-thin ceramic coatings are typically deposited as barrier coatings on polymeric substrates without significantly sacrificing the mechanical flexibility of the film. The ceramic coating is typically deposited by gas phase deposition, and different deposition techniques or parameter settings will result in varying microstructures, which in



turn yield ceramic coatings with various degrees of barrier properties (see for example, A.G.Erlat et.al, Thin Solid Films, 388, 78-86, 2001).

Whilst such technology has long been used in the food packaging industry, it is desired to obtain a substrate film with barrier properties a few orders of

5 magnitude better than those required and achieved in food packaging.

Conventional methods for optimizing the gas phase deposition techniques for the ceramic oxide layer tend to result in the production of pinholes and grain boundaries in the ceramic coating. To overcome these deficiencies, the most widely explored approach is to produce multi-layer composite films. Such multi-  
10 layer composite films, typically consist of a base substrate of polymeric material and a ceramic coating typically formed of nitrides and/or oxides of silicon and aluminium. It has been reported that the barrier properties of such multi-layer composite films may be suitable for some OLED applications (see for example J.D.Affinito, W.A.Kennewick, "Environmental Barrier Materials for Organic Light  
15 Emitting Device" US Patent, 626895, 1998).

A further conventional method of improving the barrier properties of multi-layer composite films is to apply a compliance interlayer, typically a thin polymer coating, between the layers to produce a multi-layer composite film. However, pinholes and grain boundaries (in the case of polycrystalline structures) still  
20 exist in the ceramic coating. These pinholes and grain boundaries in the ceramic coating are believed to be the dominant leakage pathway for permeation of moisture and gas molecules. Furthermore, residual stresses are inherently present in these ceramic coatings.

In view of the foregoing problems with conventional processes and devices, a need exists for an easily applied method for producing multi-layer composite films with good barrier properties without reducing production yield or compromising performance.

5    **Summary of the Invention**

In general, in a first aspect, the invention comprises a method for forming a multi-layer composite film comprising the steps of:

          depositing a barrier layer of ceramic material on a substrate; and

          applying a gas plasma process to said barrier layer.

- 10   One or more further barrier layers of ceramic material may be applied to said substrate and these layers may also be subjected to a gas plasma process.

In a second aspect there is provided a flexible electronics device formed according to the above method.

- 15   In a third aspect there is provided a display, such as an organic light emitting device (OLED) display, a liquid crystal device display, or a plastic electronic device with a display formed according to the above method.

In a fourth aspect there is provided a multi-layer composite film formed according to the above method.

- 20   In a fifth aspect there is provided a multi-layer composite film comprising:

          a substrate; and

          a barrier layer of ceramic material formed on said substrate, said barrier layer being enriched with a gas from a gas plasma.

In general terms, in one or more preferred embodiments of the present invention the gas enriched barrier layer serves to inhibit moisture and oxygen from permeating the barrier layer.

The gas plasma treatment method is preferably applied to the surface of the barrier layer of ceramic material to improve the barrier against moisture and oxygen permeation. If the ceramic material is  $\text{Al}_x\text{O}_y$  and an oxygen plasma treatment is applied thereto, this will result in an enriched oxygen layer at the surface of the ceramic coating. The incorporation of oxygen plasma into the  $\text{Al}_x\text{O}_y$  surface serves to block some of the 'pinholes' or 'leakage paths' in the ceramic coating, thus creating a more densely packaged surface layer. This is achieved by the reaction of plasma-induced oxygen with surplus aluminium in the ceramic layer.

In a preferred embodiment, the use of a gas plasma treatment method may be applied to all layers of the ceramic coating in the multi-layered composite film to enhance the barrier against moisture and oxygen permeation.

Preferably, the gas plasma treatment to the surface of the ceramic coating does not affect the optical transparency of the composite films.

Preferably, the application of the gas plasma treatment to the surface of the ceramic coating layer does not increase the thickness and the residual stress of the film.

It is particularly advantageous if, in the fabrication of the multi-layered composite film, the initial barrier layer and the further barrier layers of the ceramic coating are applied/deposited using different deposition techniques (such as RF sputtering or PECVD), or using different parameter settings (such

as deposition power or rate), or if different ceramic coating materials (such as  $\text{Al}_x\text{O}_y$  or  $\text{Si}_x\text{N}_y$ ) be used to optimize the structure and design of the barrier.

In a preferred embodiment, the multi-layered composite film comprises a polymer substrate, such as polyethylene terephthalate (PET) or polyethylene  
5 naphthalate (PEN), and layers of ceramic coating, such as aluminium oxide ( $\text{Al}_x\text{O}_y$ ) & silicon nitride ( $\text{Si}_x\text{N}_y$ ), and optionally an organic interlayer, such as glycidyl-methacrylate (GMA) or polybutyldiacrylate (PBDA), as an in-between layer.

Preferably, a gas, such as oxygen  $\text{O}_2$  or nitrogen  $\text{N}_2$ , be used in the gas plasma  
10 treatment method applied to the surface of the ceramic coating, which may be  $\text{Al}_x\text{O}_y$  or  $\text{Si}_x\text{N}_y$ , to improve the barrier against moisture and oxygen permeation.

The present invention enables a mechanically flexible substrate to be formed which is particularly advantageous for use in flexible electronics devices and displays, such as organic light emitting device (OLED) displays, liquid crystal  
15 device (LCD) displays, and plastic electronic devices with displays, for example electronic cards and smart cards.

The method according to embodiments of the present invention is a very simple process which may be easily incorporated into existing techniques for forming multi-layer composite films.

**Brief description of the drawings**

Preferred features of the invention will now be described, for the sake of illustration only, with reference to the following Figures in which:

- Figure 1 is a schematic cross-section through a conventional multi-layer composite film;
- Figure 2 is a schematic cross-section through an alternative conventional multi-layer composite film including an organic interlayer;
- Figure 3 is a schematic cross-section through an alternative conventional multi-layer composite film including two ceramic layers and an organic interlayer;
- Figure 4 is a schematic cross-section through an alternative conventional multi-layer composite film including two ceramic layers;
- Figure 5 is a schematic cross-section through an alternative conventional multi-layer composite film including one ceramic layer and an organic interlayer;
- Figure 6 is a graph showing the ratio of oxygen to aluminium against treatment time for untreated films and films treated according to an embodiment of the invention; and
- Figure 7 is a graph showing the water vapor transmission rate (WVTR) of untreated films and films treated according to an embodiment of the invention.

**Detailed Description of Preferred Embodiments**

- Figures 1 to 5 show various conventional multi-layer composite films to which the methods illustrating embodiments of the present invention may be applied. The elements of the films illustrated in Figures 1 to 5 which correspond throughout are allotted the same reference numerals.

Figure 1 shows a typical multi-layer composite film consisting of a polymer substrate 101, a first ceramic coating layer 102 deposited on the substrate 101, and a further layer of ceramic coating 102' deposited on the first ceramic coating layer 102. The number of layers of ceramic coating applied is  
5 dependent on the barrier performance required.

Figure 2 shows an alternative construction of a multi-layer composite film comprising a polymer substrate 101 onto which is deposited a first ceramic coating layer 102. An organic interlayer 103 is formed on the first ceramic coating layer 102 and a further layer of ceramic coating 102' is deposited  
10 thereon. Again, the number of layers of ceramic coating applied is dependent on the barrier performance required.

A further alternative composition of a multi-layered composite film is shown in Figure 3. A polymer substrate 101 is sandwiched between a first ceramic coating layer 102 and a further ceramic coating layer 102'. An organic  
15 interlayer 103 is deposited on the further ceramic coating layer 102' and another layer of ceramic coating 102'' is deposited on the organic interlayer 103.

Figure 4 shows another alternative composition of a multi-layered composite film including a polymer substrate 101 sandwiched between a first ceramic coating layer 102 and a further ceramic coating layer 102'.

20 A further alternative composition of a multi-layered composite film is shown in Figure 5. The film comprises a polymer substrate 101, a first ceramic coating layer 102 deposited thereon and an organic interlayer 103 formed on the first ceramic coating layer 102.

The polymer substrate material 101 used to form the films described herein and illustrated in Figures 1 to 5 is preferably polyethylene terephthalate (PET). The thickness of the PET used is preferably 200  $\mu\text{m}$  which is obtainable commercially. Other possible polymer substrate materials may be used, for example, polyethersulfone (PES) and polycarbonate (PC).

Aluminium oxide ( $\text{Al}_x\text{O}_y$ ) may be used for the ceramic coating layers 102, 102', 102''. The ceramic coating may be deposited by various deposition techniques such as Plasma Enhanced Chemical Vapor Deposition (PECVD) and Radio Frequency (RF) sputtering. RF sputtered  $\text{Al}_x\text{O}_y$  is preferably used for the multi-layer structure. The thickness of the sputtered  $\text{Al}_x\text{O}_y$  is preferably 80nm. This thickness is selected after conducting experiments to measure the water vapor transmission rate (WVTR) of single layer  $\text{Al}_x\text{O}_y$  on PET as a function of the thickness of  $\text{Al}_x\text{O}_y$ .

The organic interlayer 103 may comprise Glycidyl-methacrylate (GMA) having a preferred thickness of 400nm. Techniques such as spin coating, thermal evaporation or plasma polymerization may be used to deposit the organic interlayer 103. In the multi-layer structure shown in the figures and described herein a plasma polymerized GMA is used. Other possible plasma polymerizable materials may be used, for example, methyl methacrylate (MMA), butyl methacrylate (BMA) and heptafluorobutyl acrylate (HFBA). The organic interlayer 103 may alternatively comprise a PVD material such as one belonging to the chemical family poly-para-xylylene, for example the material commercially marketed as 'parylene'.

The conventional structures illustrated in Figures 1 to 5 are designed to improve the barrier properties of multi-layer composite films. However, despite the deposition techniques currently used for the deposition of the ceramic coating layers 102, 102', 102'', pinholes and grain boundaries will still be present in the ceramic coating. These pinholes and grain boundaries in the ceramic coating are believed to be the dominant leakage pathway for permeation of moisture and gas molecules. Furthermore, residual stresses are inherently present in these ceramic coatings.

The method according to a preferred embodiment of the invention may be applied, for example, to any one of the film structures shown in Figures 1 to 5 and comprises applying a gas plasma treatment to one or more of the ceramic layer(s) 102, 102', 102'' to improve the barrier properties of the ceramic coating layer(s). The effect of the plasma on the ceramic layer(s) is to assist in blocking some or all of the existing pinholes or leakage paths in the ceramic layer(s), thereby creating a more densely packaged surface layer. This is achieved by the plasma-induced gas reacting with surplus metal in the ceramic layer material to form additional ceramic material, such as  $Al_xO_y$  in the example where the ceramic material is  $Al_xO_y$  and the gas used in the plasma treatment is oxygen.

In fabrication of the multi-layer composite films embodying the present invention and the methods for their production, the gas plasma treatment is preferably performed after each deposition of a ceramic coating layer 102, 102', 102''.

Thus, for the structure shown in Figure 1, gas plasma treatment is applied after the initial ceramic coating layer 102 is deposited on the PET substrate 101. A

further layer of ceramic coating 102' is then deposited and this further layer 102' is then treated with gas plasma treatment.

If  $\text{Al}_x\text{O}_y$  (for example  $\text{Al}_2\text{O}_3$ ) is used as the ceramic coating layer(s) 102, 102', 102'', it is preferable to apply an oxygen plasma treatment to the ceramic

5 layer(s) to enrich the oxygen content of the ceramic coating layer(s). The oxygen plasma treatment may be performed on the oxide surface preferably under the following conditions:

RF power = 100W

oxygen flow rate = 60sccm

10 treatment time = 30min.

The oxygen plasma treatment results in an enriched oxygen layer on the ceramic coating layer(s) 102, 102', 102''.

It should be noted that the method embodying the invention is not limited to oxygen plasma, but the use of other gases such as nitrogen is also possible.

15 In a further preferred embodiment, the initial layer of ceramic coating 102 and the further layer(s) 102', 102'' of the ceramic coating may be deposited using different deposition techniques such as RF sputtering or PECVD. Also, different parameter settings, such as the power used to deposit the ceramic layers or the rate at which the layers are deposited may be used. In a further  
20 preferred embodiment, different ceramic coating materials (for example,  $\text{Al}_x\text{O}_y$  or  $\text{Si}_x\text{N}_y$ ) may be used. All of these features may be varied and serve to optimize the structure and design of the barrier film.

Figure 6 shows the ratio, at the surface of the ceramic layer material, of oxygen to aluminium varying as the surface is etched away, that is the variation of the

ratio with depth into the material for untreated  $\text{Al}_x\text{O}_y$  films and  $\text{Al}_x\text{O}_y$  films treated with an oxygen plasma according to an embodiment of the invention, as determined by X-ray photoelectron spectroscopy (XPS). The oxygen plasma  $\text{Al}_x\text{O}_y$  is used as the ceramic layer deposited on a PET substrate.

5 Figure 6 shows that the oxygen plasma treatment has enriched the oxygen content at the surface of the ceramic layer. The effect of the plasma on the ceramic layer is to assist in blocking some or all of the existing pinholes or leakage paths in the ceramic layer, thereby creating a more densely packaged surface layer. This is achieved by the oxygen reacting with surplus aluminium  
10 in the ceramic  $\text{Al}_x\text{O}_y$  layer to form additional  $\text{Al}_x\text{O}_y$ .

Figure 7 is a graph showing the water vapor transmission rate (WVTR) of untreated films and films treated according to an embodiment of the invention. The WVTR measurement for the single layer  $\text{Al}_x\text{O}_y$  of the films which received the oxygen plasma treatment showed a remarkable improvement in the barrier  
15 property, as will be seen from Figure 7, without affecting the optical transmission.

The application of the gas plasma treatment to the surface of the ceramic coating layer is considered to be particularly advantageous as no change, such as deformation or warping, in the film was observed, and therefore there is no  
20 increase the residual stress or thickness of the film.

The systems and methods according to the present invention may be particularly useful in the production of devices such as flexible electronics devices and displays, for example, organic light emitting device (OLED) displays, liquid crystal device displays (LCDs), and plastic electronic devices

with displays, such as electronic cards and smart cards having displays for displaying the information stored in the card.

Various modifications to the embodiments of the present invention described above may be made. For example, other materials and method steps can be  
5 added or substituted for those above. Thus, although the invention has been described above using particular embodiments, many variations are possible within the scope of the claims, as will be clear to the skilled reader, without departing from the spirit and scope of the invention.

**Claims**

1. A method for forming a multi-layer composite film comprising the steps of:

depositing a barrier layer of ceramic material on a substrate; and

5 applying a gas plasma process to said barrier layer.

2. A method according to claim 1, further comprising applying one or more further barrier layers of ceramic material to said substrate and/or said barrier layer.

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3. A method according to claim 2, further comprising applying a gas plasma process to one or more of said further barrier layers.

4. A method according to claim 2, wherein the step of depositing said

15 barrier layer comprises applying a first deposition process, and the step of depositing said one or more further barrier layers comprises applying one or more second deposition processes, wherein said first deposition process differs from said second deposition process.

20 5. A method according to claim 2, wherein the step of applying said one or more further barrier layers comprises applying one or more differing deposition techniques.

6. A method according to claim 1, wherein the step of depositing said barrier layer comprises applying an RF sputtering process.

7. A method according to claim 1, wherein the step of depositing said  
5 barrier layer comprises applying a Plasma Enhanced Chemical Vapor  
Deposition (PECVD) process.

8. A method according to claim 2, wherein the step of depositing said one  
or more further barrier layers comprises applying a Radio Frequency (RF)  
10 sputtering process.

9. A method according to claim 2, wherein the step of depositing said one  
or more further barrier layers comprises applying a Plasma Enhanced Chemical  
Vapor Deposition (PECVD) process.

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10. A method according to claim 2, wherein the step of depositing said  
barrier layer comprises applying a first deposition process at a first rate and/or  
power, and the step of depositing said one or more further barrier layers  
comprises applying one or more second deposition processes at a second rate  
20 and/or power, wherein said first rate and/or power differs from said second rate  
and/or power.

11. A method according to claim 2, wherein the step of depositing said  
barrier layer comprises applying a first ceramic coating material, and the step of

depositing said one or more further barrier layers comprises applying one or more second ceramic coating materials, wherein said first ceramic coating material differs from said second ceramic coating material.

5 12. A method according to claim 1, wherein the step of depositing said barrier layer comprises applying a layer of aluminium oxide ( $\text{Al}_x\text{O}_y$ ).

13. A method according to claim 1, wherein the step of depositing said barrier layer comprises applying a layer of silicon nitride ( $\text{Si}_x\text{N}_y$ ).

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14. A method according to claim 2, wherein the step of depositing said one or more further barrier layers comprises applying one or more layers of aluminium oxide ( $\text{Al}_x\text{O}_y$ ).

15 15. A method according to claim 2, wherein the step of depositing said one or more further barrier layers comprises applying one or more layers of silicon nitride ( $\text{Si}_x\text{N}_y$ ).

16. A method according to claim 1 further comprising the step of forming said  
20 substrate of a polymeric material.

17. A method according to claim 16 wherein the step of forming said substrate comprises forming said substrate of polyethylene terephthalate (PET).

18. A method according to claim 16 wherein the step of forming said substrate comprises forming said substrate of polyethylene naphthalate (PEN).

19. A method according to claim 16 wherein the step of forming said  
5 substrate comprises forming said substrate of polyethersulfone (PES).

20. A method according to claim 16 wherein the step of forming said substrate comprises forming said substrate of polycarbonate (PC).

10 21. A method according to claim 1, further comprising the step of forming an organic interlayer on said barrier layer.

22. A method according to claim 2, further comprising the step of forming an organic interlayer between said barrier layer and one or more of said one or  
15 more further barrier layers.

23. A method according to claim 22, wherein the step of forming an organic interlayer comprises forming a layer of glycidyl-methacrylate (GMA).

20 24. A method according to claim 22, wherein the step of forming an organic interlayer comprises forming a layer of polybutyldiacrylate (PBDA).

25. A method according to claim 22, wherein the step of forming an organic interlayer comprises forming a layer of methyl methacrylate (MMA).

26. A method according to claim 22, wherein the step of forming an organic interlayer comprises forming a layer of butyl methacrylate (BMA).

27. A method according to claim 22, wherein the step of forming an organic  
5 interlayer comprises forming a layer of heptafluorobutyl acrylate (HFBA).

28. A method according to claim 22, wherein the step of forming an organic interlayer comprises forming a layer of polymeric material, the polymeric material being in the chemical family poly-para-xylylene.

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29. A method according to claim 1, wherein the step of applying a gas plasma process to said barrier layer comprises applying an oxygen plasma process to the surface of the barrier layer.

15 30. A method according to claim 1, wherein the step of applying a gas plasma process to said barrier layer comprises applying a nitrogen plasma process to the surface of the barrier layer.

31. A method according to claim 4, wherein the step of applying a gas  
20 plasma process to one or more of said further barrier layers comprises applying an oxygen plasma process.

32. A method according to claim 4, wherein the step of applying a gas plasma process to one or more of said further barrier layers comprises applying a nitrogen plasma process.

5 33. A flexible electronics device formed according to the method of claim 1.

34. A display formed according to the method of claim 1.

35. An organic light emitting device (OLED) display formed according to the  
10 method of claim 1.

36. A liquid crystal device display (LCD) formed according to the method of claim 1.

15 37. A plastic electronic device with a display formed according to the method of claim 1.

38. A multi-layer composite film formed according to the method of claim 1.

20 39. A multi-layer composite film comprising:  
a substrate;  
a barrier layer of ceramic material formed on said substrate; said barrier layer being enriched with a gas from a gas plasma.

40. A multi-layer composite film according to claim 39, further comprising one or more further barrier layers of ceramic material formed on said substrate and/or said barrier layer.

5 41. A multi-layer composite film according to claim 40, wherein said one or more further barrier layers are enriched with a gas from a gas plasma.

42. A multi-layer composite film according to claim 40, wherein said barrier layer and said one or more further barrier layers are deposited using different  
10 deposition techniques.

43. A multi-layer composite film according to claim 40, wherein said one or more further barrier layers are deposited using one or more differing deposition techniques.

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44. A multi-layer composite film according to claim 39, wherein said barrier layer is deposited using an RF sputtering process.

45. A multi-layer composite film according to claim 40, wherein said one or  
20 more further barrier layers are deposited using an RF sputtering process.

46. A multi-layer composite film according to claim 39, wherein said barrier layer is deposited using a Plasma Enhanced Chemical Vapor Deposition (PECVD) process.

47. A multi-layer composite film according to claim 40, wherein said one or more further barrier layers are deposited using a Plasma Enhanced Chemical Vapor Deposition (PECVD) process.

5 48. A multi-layer composite film according to claim 40, wherein said barrier layer is applied using a first deposition technique at a first rate and/or power, and said one or more further barrier layers are applied at a second rate and/or power, wherein said first rate and/or power differs from said second rate and/or power.

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49. A multi-layer composite film according to claim 40, wherein said barrier layer comprises a first ceramic coating material, and said one or more further barrier layers comprise one or more second ceramic coating materials, wherein said first ceramic coating material differs from said second ceramic coating  
15 material.

50. A multi-layer composite film according to claim 39, wherein said barrier layer comprises aluminium oxide ( $\text{Al}_x\text{O}_y$ ).

20 51. A multi-layer composite film according to claim 39, wherein said barrier layer comprises silicon nitride ( $\text{Si}_x\text{N}_y$ ).

52. A multi-layer composite film according to claim 40, wherein said one or more further barrier layers comprise aluminium oxide ( $\text{Al}_x\text{O}_y$ ).

53. A multi-layer composite film according to claim 40, wherein said one or more further barrier layers comprise silicon nitride ( $\text{Si}_x\text{N}_y$ ).

54. A multi-layer composite film according to claim 39, wherein said  
5 substrate is formed of a polymeric material.

55. A multi-layer composite film according to claim 39 wherein said substrate comprises polyethylene terephthalate (PET).

10 56. A multi-layer composite film according to claim 39 wherein said substrate comprises polyethylene naphthalate (PEN).

57. A multi-layer composite film according to claim 39, further comprising an organic interlayer formed on said barrier layer.

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58. A multi-layer composite film according to claim 39, further comprising an organic interlayer formed between said barrier layer and one or more of said one or more further barrier layers.

20 59. A multi-layer composite film according to claim 57, wherein said organic interlayer comprises glycidyl-methacrylate (GMA).

60. A multi-layer composite film according to claim 57, wherein said organic interlayer comprises polybutyldiacrylate (PBDA).

61. A multi-layer composite film according to claim 39, wherein said barrier layer is enriched with oxygen.

62. A multi-layer composite film according to claim 39, wherein said barrier  
5 layer is enriched with nitrogen.

63. A multi-layer composite film according to claim 40, wherein one or more of said one or more further barrier layers are enriched with oxygen.

10 64. A multi-layer composite film according to claim 40, wherein one or more of said further barrier layers are enriched with nitrogen.

65. A flexible electronics device comprising the multi-layer composite film according to claim 39.

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66. A display comprising the multi-layer composite film according to claim 39.

67. An organic light emitting device (OLED) display comprising the multi-layer composite film according to claim 39.

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68. A liquid crystal device (LCD) display comprising the multi-layer composite film formed according to claim 39.

69. A plastic electronic device with a display comprising the multilayer composite film formed according to claim 39.