

#### US008963421B2

# (12) United States Patent Leu et al.

# (10) Patent No.: US 8,963,421 B2 (45) Date of Patent: Feb. 24, 2015

# (54) ELECTROLUMINESCENT DEVICE INCLUDING MOISTURE BARRIER LAYER

(75) Inventors: **Jihperng Leu**, Taipei (TW); **Shu-Hao Syu**, New Taipei (TW); **Hung-En Tu**,
Chiayi (TW); **Chih Wang**, Taichung

(TW)

(73) Assignee: National Chiao Tung University,

Hsinchu (TW)

(\*) Notice: Subject to any disclaimer, the term of this

patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

(21) Appl. No.: 13/616,442

(22) Filed: Sep. 14, 2012

(65) Prior Publication Data

US 2014/0077691 A1 Mar. 20, 2014

(51) **Int. Cl.** 

**H05B 33/12** (2006.01)

(52) U.S. Cl.

(58) Field of Classification Search

CPC ..... H01L 23/291; H01L 21/033; H01L 21/56; C23C 16/325 USPC ...... 313/498–512; 257/40, 77; 438/757

See application file for complete search history.

#### (56) References Cited

#### U.S. PATENT DOCUMENTS

4,696,796	A *	9/1987	Oka et al 422/88
6,888,172	B2	5/2005	Ghosh
7,220,687	B2	5/2007	Won
7,504,332	B2*	3/2009	Won et al 438/622
7,733,008	B2	6/2010	Ke et al.

			Weaver Padiyath et al.	313/506
$\frac{2009/0252894}{2011/0052891}$	A1 A1*	10/2009 3/2011	McCormick et al. Takahashi et al	
2011/0298361	Al*	12/2011	Matsunaga et al	313/504

### OTHER PUBLICATIONS

Chang, C.-Y., et al., Enhanced OLED performance upon photolithographic patterning by using an atomic-layer-deposited buffer layer; Organic Electronics 9:667-672 (2008).

Chen, C.W., et al., Investigation of the electrical properties and reliability of amorphous SiCN; Thin Solid Films 447-448:632-637 (2004).

Kobayashi, H., et al., Leakage current and paramagnetic defects in SiCN dielectrics for copper diffusion barriers; Applied Surface Science 254:6222-6225 (2008).

Syu, Shu-Hao, Low-temperature PECVD deposited SiCxNy/polystyrene multi-layered, high-performance moisture barrier on flexible PET film; A Thesis submitted to Department of Materials Science and Engineering-College of Engineering-National Chiao Tung University, 2012.

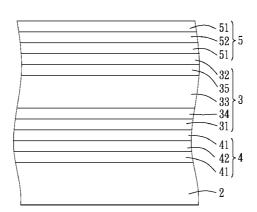
#### \* cited by examiner

Primary Examiner — Tracie Y Green (74) Attorney, Agent, or Firm — SmithAmundsen LLC; Kelly J. Smith; Dennis S. Schell

#### (57) ABSTRACT

An electroluminescent device includes: a substrate; an electroluminescent layered structure disposed over the substrate and including first and second electrode layers and an electroluminescent material layer disposed between the first and second electrode layers; and a moisture barrier layer in contact with the electroluminescent layered structure for preventing moisture from diffusing into the electroluminescent layered structure. The moisture barrier layer includes at least two inorganic films of a silicon-nitrogen-containing compound and at least one polymer film interposed between the inorganic films.

### 10 Claims, 3 Drawing Sheets



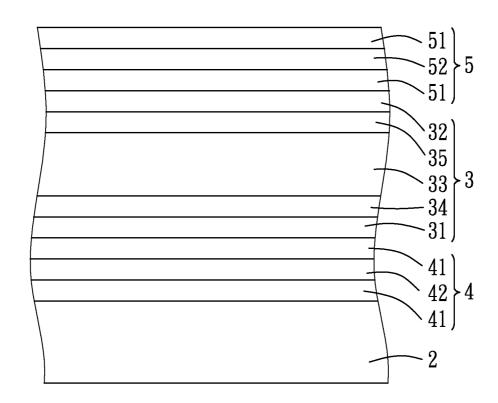


FIG. 1

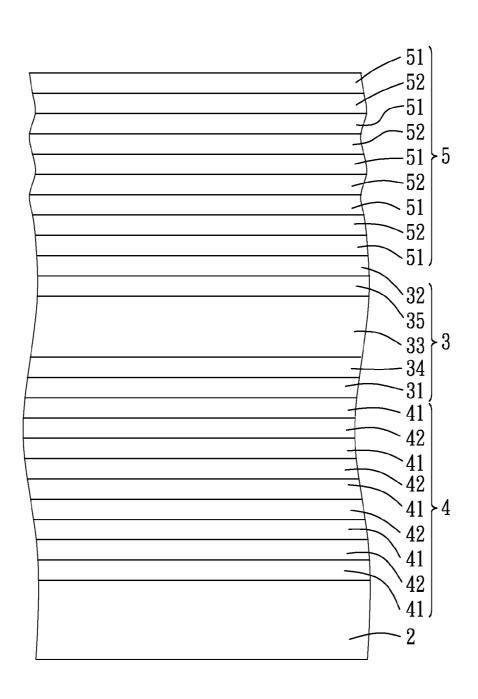


FIG. 2

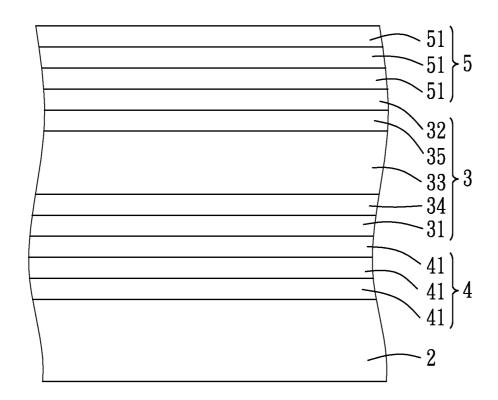


FIG. 3

# ELECTROLUMINESCENT DEVICE INCLUDING MOISTURE BARRIER LAYER

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to an electroluminescent device, more particularly to an electroluminescent device including at least one moisture barrier layer having inorganic films and optionally at least one polymer film interposed between two of the inorganic films.

## 2. Description of the Related Art

U.S. Pat. No. 7,733,008 discloses an organic light emitting diode (OLED) that includes a substrate, an anode formed on the substrate, a first moisture barrier layer formed on the 15 anode, a hole transport layer formed on the first moisture barrier layer, an electroluminescent layer formed on the hole transport layer, a second moisture barrier layer formed on the electroluminescent layer, a cathode formed on the second moisture barrier layer, and an encapsulation layer encapsulating at least partially all of these layers. The thickness of the first and second moisture barrier layers ranges from 1 nm to 20 nm. The first and second moisture barrier layers are made from a polymer selected from polyimide, TEFLON®, and parylene, and have a water vapor transmission rate (WVTR) ranging from 0.1 g/m²/day to 50 g/m²/day at 95% RH (Relative Humidity) and 39° C.

U.S. Pat. No. 7,220,687 discloses an OLED that includes a substrate, an anode formed on the substrate, an organic polymer material layer formed on the anode and having a hole 30 transport film and an emissive film, a cathode formed on the organic polymer material layer, and an encapsulation layer deposited on the cathode. The thickness of the encapsulation layer ranges from 50 nm to 2000 nm. The encapsulation layer can be made from silicon nitride (Si<sub>3</sub>N<sub>4</sub>), silicon dioxide 35  $(SiO_2)$ , or silicon oxynitride  $(SiO_xN_v)$ . Formation of the encapsulation layer is performed by introducing precursor sources together with hydrogen into a deposition chamber during chemical vapor deposition. The introduction of hydrogen into the deposition chamber can improve the WVTR of 40 the encapsulation layer thus formed from about  $1 \times 10^{-2}$  g/m<sup>2</sup>/ day (without hydrogen) to about a range between 1×10<sup>-3</sup>  $g/m^2/day$  and  $1\times10^{-4}$   $g/m^2/day$  (with hydrogen) at 90% RH and 38° C. Although the use of hydrogen can reduce the WVTR of the encapsulation layer, the manufacturing costs of 45 the OLED may be considerably increased due to the use of hydrogen in the manufacturing process.

#### SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide an electroluminescent device that can overcome the aforesaid drawback associated with the prior art.

According to one aspect of this invention, there is provided an electroluminescent device that comprises: a substrate; an selectroluminescent layered structure disposed over the substrate and including first and second electrode layers and an electroluminescent material layer disposed between the first and second electrode layers; and a moisture barrier layer in contact with the electroluminescent layered structure for preventing moisture from diffusing into the electroluminescent layered structure. The moisture barrier layer includes at least two inorganic films of a silicon-nitrogen-containing compound and at least one polymer film interposed between the inorganic films.

According to another aspect of this invention, there is provided an electroluminescent device that comprises: a sub2

strate; an electroluminescent layered structure disposed over the substrate and including first and second electrode layers and an electroluminescent material layer disposed between the first and second electrode layers; and a moisture barrier layer in contact with the electroluminescent layered structure for preventing moisture from diffusing into the electroluminescent layered structure. The moisture barrier layer includes a plurality of inorganic films of silicon carbonitride. The inorganic films are stacked one above another. Assembly of the inorganic films has a water vapor transmission rate of less than  $1 \times 10^{-2}$  g/m²/day at 75% RH and 25° C.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate embodiments of the invention, FIG. 1 is a schematic diagram of the first preferred embodiment of an electroluminescent device according to the present invention:

FIG. 2 is a schematic diagram of the second preferred embodiment of an electroluminescent device according to the present invention; and

FIG. 3 is a schematic diagram of the third preferred embodiment of an electroluminescent device according to the present invention.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before the present invention is described in greater detail with reference to the accompanying preferred embodiments, it should be noted herein that like elements are denoted by the same reference numerals throughout the disclosure.

FIG. 1 illustrates the first preferred embodiment of an electroluminescent device 100 according to the present invention. The electroluminescent device 100 can be an OLED, and includes: a substrate 2; an electroluminescent layered structure 3 disposed over the substrate 2 and including first and second electrode layers 31, 32 and an electroluminescent material layer 33 disposed between the first and second electrode layers 31, 32; a first moisture barrier layer 4 in contact with the electroluminescent layered structure 3 for preventing moisture from diffusing into the electroluminescent layered structure 3; and a second moisture barrier layer 5 disposed over the electroluminescent layered structure 3. The first moisture barrier layer 4 is interposed between the substrate 2 and the electroluminescent layered structure 3. The electroluminescent layered structure 3 is interposed between the first and second moisture barrier layers 4, 5 so that environmental moisture can be prevented from diffusing from two opposite sides of the electroluminescent layered structure 3 into the electroluminescent layered structure 3.

The electroluminescent layered structure 3 further includes a hole transporting layer 34 interposed between the first electrode layer 31 and the electroluminescent material layer 33, and an electron injection layer 35 interposed between the second electrode layer 32 and the electroluminescent material layer 33.

Each of the first and second moisture barrier layers 4, 5 includes at least two inorganic films 41, 51 of a siliconnitrogen-containing compound and at least one polymer film 42, 52 interposed between the inorganic films 41, 51.

In this embodiment, the silicon-nitrogen-containing compound is silicon carbonitride ( $SiC_xN_y$ ). Preferably, the amount of silicon in the silicon carbonitride ranges from 30 to 52 atomic %, the amount of carbon in the silicon carbonitride ranges from 37 to 56 atomic %, and the amount of nitrogen in the silicon carbonitride ranges from 11 to 14 atomic %.

Preferably, the polymer film **42**, **52** is made from a plasma polymerized polymer selected from polystyrene, polymethacrylate and polymethylmethacrylate.

Preferably, the substrate **2** is flexible, and is made from a material selected from polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulfone and polyimide (PI).

In this embodiment, the first and second electrode layers 31, 32 are in contact with the first and second moisture barrier layers 4, 5, respectively.

Preferably, each of the inorganic films 41, 51 has a layer thickness ranging from 100 nm to less than 1000 nm and the polymer film 42, 52 has a layer thickness ranging from 100 nm to less than 1000 nm. The layer thicknesses of the inorganic films 41, 51 and the polymer film 42, 52 may vary according to the actual requirements.

Formation of each of the first and second moisture barrier layers 4, 5 is preferably performed by plasma enhanced chemical vapor deposition (PECVD). The first and second moisture barrier layers 4, 5 thus formed can exhibit a WVTR of less than  $1\times10^{-2}$  g/m²/day at 75% RH and 25° C., and a pin-hole density of less than 35/0.0379 mm². It is noted that the pin-hole density has a proportional relationship with the water vapor transmission rate.

Formation of the inorganic films **41**, **51** is performed by introducing an inorganic source precursor into a PECVD reactor (not shown). Formation of the polymer film **42**, **52** is performed by introducing a polymer source precursor into the PECVD reactor.

Examples of the inorganic source precursors for forming the silicon-nitrogen-containing compound in the PECVD reactor include 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilane ( $C_9H_{21}N_3Si_3$ , VSZ), bis(dimethylamino)diethylsilane, N,N-dimethyltrimethylsilylamine, and N-methyl-aza-trimethylsilacyclopentane.

Preferably, formation of the inorganic films **41**, **51** of the silicon-nitrogen-containing compound through PECVD is conducted at a substrate temperature ranging from room temperature to about 300° C. Table 1 shows the relation between the composition of each of the inorganic films **41**, **51** of SiC<sub>x</sub>N<sub>y</sub>, and the substrate temperature used in forming the inorganic films **41**, **51** of SiC<sub>x</sub>N<sub>y</sub>, in the PECVD process.

TABLE 1

substrate	Composition, atomic %				
emperature, ° C.	Si	С	N		
25	30.5	55.5	14.0		
100	48.6	39.5	11.9		
200	49.0	39.2	11.8		
300	51.3	37.0	11.7		

FIG. 2 illustrates the second preferred embodiment of an electroluminescent device 100 according to the present 55 invention. The second preferred embodiment differs from the previous embodiment in that each of the first and second moisture barrier layers 4, 5 includes five inorganic films 41, 51 of the silicon-nitrogen-containing compound and four polymer films 42, 52 alternately disposed with the inorganic 60 films 41, 51. Each of the polymer films 42, 52 is interposed between and is in contact with two adjacent ones of the inorganic films 41, 51.

FIG. 3 illustrates the third preferred embodiment of an electroluminescent device 100 according to the present 65 invention. The third preferred embodiment differs from the previous embodiments in that each of the first and second

4

moisture barrier layers 4, 5 includes three inorganic films 41, 51 of the silicon-nitrogen-containing compound, which are stacked one above another. The polymer film 42, 52 is omitted in this embodiment. Assembly of the inorganic films 41, 51 has a water vapor transmission rate (WVTR) of less than  $1 \times 10^{-2}$  g/m<sup>2</sup>/day at 75% RH and 25° C.

The following examples and comparative examples are provided to illustrate the preferred embodiments of the invention, and should not be construed as limiting the scope of the invention.

#### **EXAMPLE**

#### Example 1(E1)

Forming a SiC<sub>x</sub>N<sub>y</sub>/Polystyrene (PS)/SiC<sub>x</sub>N<sub>y</sub> Moisture Barrier Layer on a Substrate

A polyethylene terephthalate (PET) substrate was used as 20 a deposition substrate and was mounted on a back plate in a PECVD reactor (not shown). The electrode spacing of the PECVD reactor was 20 mm. 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilane (C<sub>9</sub>H<sub>21</sub>N<sub>3</sub>Si<sub>3</sub>, VSZ) was stored in a VSZ-storing container and was heated to generate a VSZ vapor that was used as a  $SiC_xN_v$  source precursor. The  $SiC_xN_v$  source precursor was continuously carried into the PECVD reactor using an argon carrier gas so as to form a first SiC<sub>x</sub>N<sub>y</sub>, film having a layer thickness of 100 nm on the PET substrate. The flow rate of each of the SiC<sub>x</sub>N<sub>y</sub>, source precursor and the argon carrier gas was 20 sccm. The operating conditions of forming the first SiC<sub>x</sub>N<sub>y</sub>, film were as follows: an RF plasma was generated using an RF power of 50 W (power density=0.15 W/cm<sup>3</sup>) and was introduced into the PECVD reactor; and the reactor pressure and the substrate temperature of the PECVD reactor were maintained at about 90 mTorr and about 25° C., respectively. Styrene monomer was stored in a polymer-storing container and was heated to generate a styrene vapor that was used as a polymer source precursor. After formation of the first SiC<sub>x</sub>N<sub>y</sub>, film on the PET substrate, the polymer source precursor was continuously carried into the PECVD reactor using the argon carrier gas so as to form a polystyrene (PS) film having a layer thickness of 100 nm on the first SiC<sub>x</sub>N<sub>y</sub> film. The flow rate of each of the polymer source precursor and the argon carrier gas was 20 sccm. The operating conditions for forming the polystyrene film were the same as those for forming the first SiC<sub>x</sub>N<sub>y</sub> film. After formation of the polystyrene film on the first SiC<sub>x</sub>N<sub>y</sub>, film, the SiC<sub>x</sub>N<sub>y</sub>, source precursor was again continuously carried into the PECVD reactor using the argon carrier gas so as to form a second SiC<sub>x</sub>N<sub>y</sub> 50 film having a layer thickness of 100 nm on the polystyrene film. The flow rate of each of the  $SiC_xN_y$  source precursor and the argon carrier gas was 20 sccm for forming the second SiC<sub>x</sub>N<sub>y</sub> film. The operating conditions for forming the second SiC, N, film were the same as those for forming the first  $SiC_xN_y$  film. Assembly of the first and second  $SiC_xN_y$  films and the polymer film (i.e.,  $SiC_xN_y/PS(100 \text{ nm})/SiC_xN_y$  moisture barrier layer) thus formed has a WVTR of  $7 \times 10^{-3}$  g/m<sup>2</sup>/ day at 75% RH and 25° C.

# Example 2(E2)

Forming a SiC<sub>x</sub>N<sub>y</sub>/PS/SiC<sub>x</sub>N<sub>y</sub>, Moisture Barrier Layer on a Substrate

Preparation of the moisture barrier layer on the PET substrate for Example 2 was similar to that of Example 1 except for the layer thickness of the polystyrene film of Example 2.

The layer thickness of the polystyrene film of Example 2 is 500 nm. The SiC<sub>x</sub>N<sub>x</sub>/PS(500 nm)/SiC<sub>x</sub>N<sub>y</sub>, moisture barrier layer thus formed has a WVTR of  $3.8 \times 10^{-3}$  g/m<sup>2</sup>/day at 75% RH and 25° C.

# Example 3(E3)

# Forming a (SiC<sub>x</sub>N<sub>y</sub>/PS)<sub>4</sub>/SiC<sub>x</sub>N<sub>y</sub> Moisture Barrier Layer on a Substrate

Preparation of the moisture barrier layer on the PET substrate for Example 3 was similar to that of Example 1, except that after formation of the second  $SiC_xN_y$  film, three more  $SiC_xN_v$  films and three more polystyrene films were formed under the same operating conditions as those of Example 1. The five  $SiC_xN_v$  films and the four polystyrene films were alternatively formed. Each of the five SiC<sub>x</sub>N<sub>y</sub>, films and the four polystyrene films has a layer thickness of 100 nm. The  $(SiC_xN_y/PS)_4/SiC_xN_y$  moisture barrier layer thus formed has a WVTR of  $8\times10^{-5}$  g/m²/day at 75% RH and 25° C. The structure of  $(SiC_xN_y/PS)_4$  represents  $SiC_xN_y/PS/SiC_xN_y/P$ SiC<sub>x</sub>N<sub>x</sub>/PS/SiC<sub>x</sub>N<sub>x</sub>/PS.

#### Example 4(E4)

# Forming a SiC<sub>x</sub>N<sub>y</sub>/SiC<sub>x</sub>N<sub>y</sub>/SiC<sub>x</sub>N<sub>y</sub> Moisture Barrier Layer on a Substrate

Preparation of the moisture barrier layer on the PET substrate for Example 4 was similar to that of Example 1, except 30 that the polystyrene film was replaced by a SiC<sub>x</sub>N<sub>y</sub>, film. The three SiC, N,, films were formed successively in a manner that after forming the first SiC<sub>x</sub>N<sub>y</sub>, film, introduction of the SiC<sub>x</sub>N<sub>y</sub> source precursor, the argon carrier gas and the RF plasma into the PECVD reactor was stopped for a predetermined period 35 of time before deposition of the second SiC<sub>x</sub>N<sub>y</sub>, film and that after forming the second  $SiC_xN_y$  film, introduction of the SiC<sub>2</sub>N<sub>4</sub>, source precursor, the argon carrier gas and the RF plasma into the PECVD reactor was stopped for another SiC<sub>x</sub>N<sub>y</sub>, film. Each of the three SiC<sub>x</sub>N<sub>y</sub>, films has a layer thickness of 100 nm. The SiC<sub>x</sub>N<sub>y</sub>/SiC<sub>x</sub>N<sub>y</sub>/SiC<sub>x</sub>N<sub>y</sub> moisture barrier layer thus formed has a WVTR of  $6 \times 10^{-3}$  g/m<sup>2</sup>/day at 75% RH and 25° C., and a pin-hole density of 4/0.0379 mm<sup>2</sup>.

#### Comparative Example 1(CE1)

# Forming a $\mathrm{SiC}_x\mathrm{N}_v$ Moisture Barrier Layer on a Substrate

The moisture barrier layer of Comparative Example 1 includes solely one SiC<sub>x</sub>N<sub>y</sub> film having a layer thickness of 100 nm. The operating conditions for forming the  $SiC_xN_y$  film of Comparative Example 1 were similar to those for forming g/m<sup>2</sup>/day at 75% RH and 25° C., and a pin-hole density of  $42/0.0379 \text{ mm}^2$ 

# Comparative Example 2(CE2)

## Forming a SiC<sub>x</sub>N<sub>y</sub> Moisture Barrier Layer on a Substrate

Preparation of the moisture barrier layer on the PET sub- 65 strate of Comparative Example 2 was similar to that of Comparative Example 1, except for the layer thickness of the

6

 $SiC_xN_v$  film. The layer thickness of the  $SiC_xN_v$  film of Comparative Example 2 is 200 nm. The 200 nm SiC<sub>x</sub>N<sub>y</sub> moisture barrier layer thus formed has a WVTR of  $4 \times 10^{-2}$  g/m<sup>2</sup>/day at 75% RH and 25° C., and a pin-hole density of 35/0.0379  $mm^2$ .

By forming a plurality of the inorganic films 41, 51 and optionally at least one polymer film 42, 52 interposed between two of the inorganic films 41, 51 in the electroluminescent device 100 of this invention, the aforesaid drawback 10 associated with the prior art can be alleviated.

While the present invention has been described in connection with what are considered the most practical and preferred embodiments, it is understood that this invention is not limited to the disclosed embodiments but is intended to cover various arrangements included within the spirit and scope of the broadest interpretation and equivalent arrangements.

What is claimed is:

- 1. An electroluminescent device comprising: a substrate;
- an electroluminescent layered structure disposed over said substrate and including first and second electrode layers and an electroluminescent material layer disposed between said first and second electrode layers; and
- a first moisture barrier layer in contact with said electroluminescent layered structure for preventing moisture from diffusing into said electroluminescent layered structure:
- wherein said first moisture barrier layer includes at least two inorganic films of a silicon-nitrogen-containing compound and at least one polymer film interposed between said inorganic films;
- wherein said polymer film is made from a plasma polymerized polymer selected from polystyrene, polymethacrylate and polymethylmethacrylate;
- wherein said first moisture barrier layer has a water vapor transmission rate of less than  $1\times10^{-2}$  g/m<sup>2</sup>/day at 75% RH and 25° C.
- 2. The electroluminescent device of claim 1, wherein said predetermined period of time before deposition of the third 40 silicon-nitrogen-containing compound is silicon carboni-
  - 3. The electroluminescent device of claim 2, wherein the amount of silicon in said silicon carbonitride ranges from 30 to 52 atomic %, the amount of carbon in said silicon carbo-45 nitride ranges from 37 to 56 atomic %, and the amount of nitrogen in said silicon carbonitride ranges from 11 to 14 atomic %.
  - 4. The electroluminescent device of claim 1, wherein said substrate is made from a material selected from polyethylene 50 terephthalate, polyethylene naphthalate, polyethersulfone and polyimide.
- 5. The electroluminescent device of claim 1, further comprising a second moisture barrier layer, said first moisture barrier layer being interposed between said substrate and said the first  $SiC_xN_y$ , film of Example 1. The 100 nm  $SiC_xN_y$  55 electroluminescent layered structure, said electroluminescent layered structure being interposed between said first and second moisture barrier layers.
  - 6. The electroluminescent device of claim 5, wherein said second moisture barrier layer has a structure the same as that 60 of said first moisture barrier layer.
    - 7. The electroluminescent device of claim 5, wherein said first and second electrode layers are in contact with said first and second moisture barrier layers, respectively.
    - 8. The electroluminescent device of claim 1, wherein said substrate is flexible, said first moisture barrier layer being deposited on said substrate through plasma enhanced chemical vapor deposition.

8

- **9**. An electroluminescent device comprising:
- an electroluminescent layered structure disposed over said substrate and including first and second electrode layers and an electroluminescent material layer disposed 5 between said first and second electrode layers; and
- a moisture barrier layer in contact with said electroluminescent layered structure for preventing moisture from diffusing into said electroluminescent layered structure;
- wherein said moisture barrier layer includes a plurality of 10 inorganic films of silicon carbonitride, said inorganic films being stacked one above another; and
- wherein assembly of said inorganic films has a water vapor transmission rate of less than  $1\times10^{-2}$  g/m<sup>2</sup>/day at 75% RH and 25° C.
- 10. The electroluminescent device of claim 9, wherein the amount of silicon in said silicon carbonitride ranges from 30 to 52 atomic %, the amount of carbon in said silicon carbonitride ranges from 37 to 5 atomic %, and the amount of nitrogen in said silicon carbonitride ranges from 11 to 14 20 atomic %.

\* \* \* \* :