The invention provides devices that are conformally encapsulated using ALD and methods for producing the same.
FIELD OF THE INVENTION

The present invention relates to various devices that are conformally encapsulated using ALD and methods for producing the same.

BACKGROUND OF THE INVENTION

Thin gas diffusion barrier films are often needed to protect some components, e.g., organic components, in electronic devices. This is particularly true in photo-pumped quantum dot light emitting diodes.

Light emitting diodes (LEDs) are now used in everyday applications such as traffic signals and brake lights in automobiles, where high brightness, low power consumption and long lifetimes are highly desirable facets of the inorganic LEDs. An additional area where LEDs have been introduced is as a back light in liquid crystal displays (LCDs), where the LEDs offer the ability to switch on and off very quickly, which is a significant advantage over the more traditional cold cathode fluorescent light (CCFL) that have been used previously in very large numbers in the fabrication of LCDs.

Currently there are two possible routes to achieving white light utilizing an LED as a light source. The first method uses a blue LED comprising GaN or InGaN as the 'base' emitter, which emits at a wavelength of approximately 465 nm. As shown in Figure 3, other materials such as Ce:YAG emits at different wavelength. The LED also comprises phosphors of different colors to produce white light. A fraction of the blue light undergoes a Stokes shift, whereby a portion of the blue light is transformed from shorter wavelengths to longer wavelengths. Depending on the color of the original LED, phosphors of different colors are used to produce white light. If several phosphor layers of distinct colors are used, the emitted spectrum is broadened, effectively increasing the color rendering index (CRI).
Phosphor based LEDs have a lower efficiency than normal LEDs due to the heat loss from the Stokes shift and other phosphor-related degradation issues. As well as a relatively higher power consumption, this approach to generating white light results in a broad based spectrum, which is not ideal when coupled with discreet color filters. Applications such as LCDs utilize color filters, which possess discreet band pass characteristics, that is, incident light that lies outside of the desired band gap is 'cut off' by the filter and is therefore wasted.

In order to maximize the efficiency of a red, green and blue (RGB) LCD, it would be advantageous to 'concentrate' the component light close to the band pass of the color filters used in the fabrication of the LCD. This can be achieved by utilizing nano-crystals (NCs) or quantum dots (QDs) as the phosphor component of the LED and more specifically, red and green photo-luminescent (PL) QDs.

QDs can be incorporated as a PL material in inorganic light emitting diodes (LEDs) to create LCDs possessing improved color gamut. However, like many organic based electronic devices, the QDs and the materials used to integrate the QDs are sensitive to ambient exposure and must therefore be protected in a cost effective manner.

Insufficient protection of organic electronic devices from environmental oxidants causes device failure because oxygen and water can easily permeate through the organic materials. These oxidants degrade the light-emitting inorganic materials. In the past, inorganic materials such as SiO₂ and Al₂O₃ have been used to provide a gas diffusion barrier. Alternatively, epoxy compounds have also been used to encapsulate less sensitive inorganic components.

Organic epoxy materials may chemically interact with the QD and organic materials comprising the electronic devices. The photo-acid generators (i.e., compounds that generate an acid molecule and de-protects the resin molecules upon exposure to light) in light curable epoxy can be detrimental to acid sensitive organic materials. Thus, exposure of the QD and surrounding polymeric materials to the epoxy could decrease lifetime or immediately decrease the efficiency of the devices.

The inorganic barrier materials usually display no significant gain in permeability reduction beyond a critical thickness of about 100 Å to about 300 Å because of defects and propagation of grain boundaries. Unfortunately, single inorganic films with thicknesses of about 100 Å to about 300 Å deposited using sputtering or evaporation do not
provide an adequate gas diffusion barrier. Typical H₂O transmission rates of about 0.05 g m⁻² day⁻¹ are observed for single thin films of SiO₂ and Al₂O₃. The maximum allowable H₂O transmission rates of about 1 x 10⁻⁶ g m⁻² day⁻¹ are estimated to achieve a lifetime of 10,000 hours for completely organic electronics. Although single inorganic films prepared by sputtering can not obtain H₂O transmission rates of about 1 x 10⁻⁶ g m⁻² day⁻¹, a multilayer of many separate flexible individual inorganic layers with thicknesses of about 200 Å or less can be used to obtain lower H₂O transmission rates. The inorganic layer thickness is limited to about 200 Å or less because typically inorganic layers become brittle at thicknesses of greater than 200 Å.

[0012] Another limitation of these sputtered and evaporated films is that they are deposited by line-of-sight techniques. All sides of an object are not coated evenly or conformally. Only the areas of a device that are directly exposed to the deposition source are coated. Sputtered films are known to have pinholes because of the random nature of line-of-sight deposition when the film thickness is less than about 200 Å to about 300 Å. Without being bound by any theory, it is believed that these pinholes are responsible for the lower limit of about 0.05 g m⁻² day⁻¹ for the H₂O transmission rates of single thin inorganic gas diffusion layers. If these pinholes could be eliminated, then much better gas diffusion barriers would result from these thin inorganic films.

[0013] Accordingly, there is a need for encapsulating methods that can significantly reduce the gas diffusion rate.

SUMMARY OF THE INVENTION

[0014] Some aspects of the invention provide a light emitting diode that is conformally encapsulated with a gas barrier layer having a thickness of about 500 Å or less, typically 100 Å or less, often 50 Å or less, and more often 26 Å or less.

[0015] In some embodiments, the gas barrier layer comprises aluminum oxide.

[0016] Still in other embodiments, the light emitting diode is quantum dot light emitting diode.

[0017] Another aspect of the invention provide a light emitting diode that is encapsulated with a gas barrier layer that provides water vapor transmission rate of about 0.02 g m⁻² day⁻¹ or less as measured using a tritium tracer test.
In some embodiments, the light emitting diode is conformally encapsulated with a gas diffusion barrier layer.

Yet in other embodiments, the gas diffusion barrier layer comprises an atomic layer of aluminum oxide.

Still other aspects of the invention provide a method for producing a light emitting diode that is conformally encapsulated with a gas diffusion barrier layer. The method comprises encapsulating a light emitting diode with a gas diffusion barrier layer using an atomic layer deposition process to produce a conformally encapsulated light emitting diode.

In some embodiments, the gas diffusion barrier layer comprises aluminum oxide.

Yet in other embodiments, the gas diffusion barrier layer provides water vapor transmission rate of about 0.02 g m\(^2\) day\(^{-1}\) or less as measured using a tritium tracer test.

Yet other aspects of the invention provide an electronic device comprising a light emitting diode described herein.

In some embodiments, the light emitting diode is a quantum dot light emitting diode.

Yet in other embodiments, the electronic device comprises a display element.

Yet still other aspects of the invention provide a white light emitting quantum dot light emitting diode comprising a quantum dot light emitting diode that is conformally encapsulated with aluminum oxide.

In some embodiments, aluminum oxide encapsulation is formed by an atomic layer deposition process.

Yet in other embodiments, the quantum dot light emitting diode is a down converting quantum dot light emitting diode. The term "down converting" refers to converting a higher energy electromagnetic radiation to a lower energy electromagnetic radiation, that is absorbing electromagnetic radiation and re-emitting as a lower energy electromagnetic radiation. For example, absorbing UV light and emitting visible light.
Still yet other aspects of the invention provide a composite material comprising a layer of light emitting diode (LED); a layer of quantum dots; and a conformally encapsulating gas diffusion barrier layer. Generally, the quantum dot layer is coated onto the light emitting diode layer. Alternatively, a protective layer can be placed between the quantum dot layer and the LED layer. Conformally coating the composite material provides protection against various harmful gases such as water vapor and oxygen.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0030] Figure 1 is a schematic of a typical light emitting diode.

[0031] Figure 2 is a schematic depicting atomic layer deposition of molecular layer deposition. In each step a gas phase precursor reacts with exposed surface sites until all surface sites are consumed.

[0032] Figure 3 is a spectrum of white LED utilizing secondary inorganic phosphors.

[0033] Figure 4 is a schematic of a blue LED in conjunction with a QD containing composite that has been encapsulated using methods of the invention.

[0034] Figures 5A and B show the spectrum of white LED utilizing a red and green QD composite prior to and following ALD encapsulation, respectively.

**DETAILED DESCRIPTION OF THE INVENTION**

[0035] The invention provides various conformally gas diffusion barrier encapsulated devices and methods for producing the same. In some aspects, the invention provides methods for producing or fabricating conformal gas diffusion barriers. Such conformal gas diffusion barrier can comprise inorganic, organic and/or hybrid materials. Typically, these gas diffusion barriers are produced using atomic layer deposition (ALD) and/or molecular layer deposition (MLD) to conformally encapsulate various electronic devices and/or components. Exemplary electronic devices and/or components that are suitable for processes of the invention include, but are not limited to, QD LEDs, such as photo-pumped quantum dot light emitting diodes, and devices comprising the same.

[0036] In some aspects, methods of the invention include using a single ALD layer as a conformally encapsulated gas diffusion barrier layer for protection of the device, such as photo-pumped QD LED device. Such conformally encapsulated devices are protected from a variety of environmental gases including, but not limited to, H₂O and O₂.
In other aspects, methods of the invention include using a plurality of inorganic, organic, organic/inorganic hybrid material, or a mixture thereof to produce conformally encapsulated gas diffusion barrier layer in a stack formation, for example, for protection of the photo-pumped QD LED device from H₂O and O₂ gases.

Still in other aspects, methods of the invention include using a single ALD layer as a pre-encapsulation layer to protect the device (e.g., photo-pumped QD and LED materials) from further encapsulation materials.

Yet in other aspects, methods of the invention include using a plurality of inorganic, organic, hybrid material, or a mixture thereof to produce a stack formation barrier as a pre-encapsulation layer to protect the device (e.g., photo-pumped QD and LED materials) from further encapsulation materials.

These ALD coatings result in superior gas diffusion barrier properties compared to conventional gas diffusion barrier methods and substantially reduce the rate of device degradation.

The invention will now be described with respect to encapsulating QD LEDs. However, it should be appreciated that the scope of the invention is not limited to such devices. In general, the scope of the invention encompasses any device in which a gas diffusion barrier is desired.

The components of an LED are shown in Figure 1. The luminescent portion of an LED is a semiconductor diode that emits incoherent narrow-spectrum light when electrically biased. The electroluminescent diode is a small portion of the LED. The other components consist of the electrical leads, through which the bias is applied, and a lens to focus the emitting light and protect the diode. Often, a reflector is also added behind the diode to further focus the light.

The color of the emitted light depends on the semiconducting materials used and can range from infrared to ultraviolet. The maximum obtainable brightness and efficiency of the diode are also materials dependent.

Photo-pumped QD LEDs use the dynamic properties of both LEDs and QDs. QDs are typically inorganic semiconductor nano-crystals that have a discrete quantized energy spectrum because of quantum confinement within the structure. Therefore, when excited they typically emit specific wavelengths dependant on their size and material
makeup. In photo-pumped QD LEDs, the LEDs are used to excite the QDs in the spectral region they absorb, and in turn the QDs efficiently output visible light. The color and the intensity of the resulting light are determined by the combination of different QDs and their efficiency. Such a system allows for modulation of light intensity, and color contrast simply by tuning the light intensity of the LED used for photo-pumping. Additionally, by mixing the QDs in the emissive layer, photo-pumped QD LEDs provide a means of making an efficient white light emitting source.

[0045] Photo-pumped QD LEDs can be configured in a number of ways: (1) the QD dispersion or film is fabricated on the outside of the lens structure; (2) the QD dispersion or film is placed between the diode and the lens structure; (3) the lens composite contains QDs (e.g., the QDs are inside the lens material); (4) the QD dispersion or film is on a screen/film that is in front of the LED device and the LED is scanned across the screen; and/or (5) the QDs are dispersed in the screen materials (e.g., the QDs are inside the screen). Regardless the configuration, in order to provide a sufficient gas barrier protection, an encapsulation needs to encapsulate entirely and conformally the sensitive QD and polymeric materials.

[0046] Atomic layer deposition (ALD) is a gas phase chemical process used to create extremely thin coatings. Typically, ALD reactions use two or more chemicals called precursors. These precursors react with a surface one-at-a-time in a sequential manner. By exposing the precursors to the growth surface repeatedly, a thin film of desired thickness can be deposited. ALD is a self-limiting, sequential surface chemistry that deposits conformal thin-films of materials onto substrates of varying compositions. ALD is similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. ALD film growth is self-limited and is based on surface reactions, which makes achieving atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, atomic layer control of film grown can be obtained as fine as about 0.1 angstroms per monolayer. ALD has many advantages over other thin film deposition techniques. For example, ALD grown films are conformal, pin-hole free, and chemically bonded to the substrate. With ALD it is possible to deposit coatings perfectly uniform in thickness inside deep trenches, porous media and around particles. The film thickness range is usually from about 1nm to about 500 nm. However, it should be appreciated that the scope of the present invention is not limited to the specific film thicknesses disclosed herein. One skilled in the art will clearly recognize that different film thickness is desired depending on the device to be
coated and the application for which the device is used. A schematic illustration of the ALD method is shown in Figure 2. For example, in one particular embodiment Al₂O₃ ALD surface chemistry is based on the sequential deposition of Al(CH₃)₃ and H₂O. The Al₂O₃ ALD surface chemistry is described by the following two sequential surface reactions:

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\begin{align*}
(1) \quad & \text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{AlO-\text{Al(CH}_3)_2}^* + \text{CH}_4 & \text{(A)} \\
(2) \quad & \text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4 & \text{(B)}
\end{align*}
\]

The surface chemistry, thin-film growth rates, and thin-film properties for Al₂O₃ ALD have been shown to deposit about 1.2 Å per AB cycle.

[0047] Unlike physical vapor deposition techniques such as sputtering or evaporation, ALD does not require line-of-sight to the substrate. Consequently, conformal and continuous films can be deposited on rough substrates. Many inorganic films can be deposited with ALD techniques. SiO₂ and Al₂O₃ ALD films can also be deposited at low temperatures that are compatible with polymeric materials or the plastic substrates used for flexible displays. Additionally, metallic materials can also be deposited by ALD methods. Other materials that can be deposited include organic and hybrid inorganic/organic materials as well as ceramics. These materials can be deposited by a technique analogous to ALD using molecular layers to fabricate polymers called molecular layer deposition (MLD).

[0048] For Al₂O₃ ALD films with thicknesses of 5 nm or greater, oxygen transmission rates were well below the MOCON instrument test limit of about 5 x 10⁻³ cc m⁻² day⁻¹. Gas diffusion barriers with a water vapor transmission rate (i.e., WVTR) of about 1 x 10⁻³ g m⁻² day⁻¹ as measured using a tritium tracer test were achieved using a single Al₂O₃ ALD coating with thicknesses of 26 nm on PEN and Kapton® substrates at room temperature. These single layer Al₂O₃ ALD films offer a dramatic improvement of 50 times compared with the sputtered Al₂O₃ films used in the previous inorganic/polymer multilayer barriers. The best WVTR reported from previous single layer Al₂O₃ films was about 0.05 g m⁻² day⁻¹. Further transmission measurements of the Ca film oxidation indicated that the WVTR was about 1.7 x 10⁻³ g m⁻² day⁻¹ at 38 °C and 85% relative humidity (RH) and about 6.5 x 10⁻⁵ g m⁻² day⁻¹ at 60 °C and 85% RH. It is believed that layers of different materials in a stack formation can further reduce the WVTR.

[0049] Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting.
EXPERIMENTAL

A composite obtained from a solution comprising green emitting QDs in toluene (0.15 cm³, 100 mg cm⁻³, peak emission 545 nm), red emitting QDs in toluene (0.15 cm³, 100 mg cm⁻³, peak emission 630 nm) and poly(methyl methacrylate) (PMMA) (0.60 cm³, 228 mg cm⁻³) was injected into the well of an LED (pre-cleaned with soldered leads) possessing a peak emission of 445 nm and the composite cured in a vacuum oven at 100 °C for 24 h. The resulting devices were transferred to an ALD reactor and exposed to 400 cycles at 200 °C. The encapsulated device is schematically illustrated in Figure 4 and the light emitting characteristics of the pre-encapsulated and post-encapsulated device are shown in Figures 5A and 5B, respectively, which show that there is no significant change in the light emitting property after encapsulation.

The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. Although the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.
What is Claimed:

1. A light emitting diode that is conformally encapsulated with a gas barrier layer having a thickness of about 500 Å or less.

2. The light emitting diode of Claim 1, wherein said gas barrier layer comprises aluminum oxide.

3. The light emitting diode of Claim 1, wherein said light emitting diode is quantum dot light emitting diode.

4. The light emitting diode of Claim 1, wherein the thickness of said gas barrier layer is about 100 Å or less.

5. The light emitting diode of Claim 1, wherein the thickness of said gas barrier layer is about 50 Å or less.

6. The light emitting diode of Claim 1, wherein the thickness of said gas barrier layer is about 26 Å or less.

7. A light emitting diode that is encapsulated with a gas barrier layer that provides water vapor transmission rate of about 0.02 g m² day⁻¹ or less as measured using a tritium tracer test.

8. The light emitting diode of Claim 7, wherein said light emitting diode is conformally encapsulated with a gas diffusion barrier layer.

9. The light emitting diode of Claim 7, wherein said gas diffusion barrier layer comprises an atomic layer of aluminum oxide.

10. A method for producing a light emitting diode that is conformally encapsulated with a gas diffusion barrier layer, said method comprising encapsulating a light emitting diode with a gas diffusion barrier layer using an atomic layer deposition process to produce a conformally encapsulated light emitting diode.

11. The method of Claim 10, wherein the gas diffusion barrier layer comprises aluminum oxide.

12. The method of Claim 10, wherein the gas diffusion barrier layer provides water vapor transmission rate of about 0.02 g m² day⁻¹ or less as measured using a tritium tracer test.

14. The electronic device of Claim 13, wherein said light emitting diode is a quantum dot light emitting diode.

15. The electronic device of Claim 13, wherein said electronic device comprises a display element.

16. A white light emitting quantum dot light emitting diode comprising a quantum dot light emitting diode that is conformally encapsulated with aluminum oxide.

17. The white light emitting quantum dot light emitting diode of Claim 16, wherein aluminum oxide encapsulation is formed by an atomic layer deposition process.

18. The white light emitting quantum dot light emitting diode of Claim 16, wherein the quantum dot light emitting diode is a down converting quantum dot light emitting diode.

19. A composite material comprising a layer of light emitting diode; a layer of quantum dots; and a conformally encapsulating gas diffusion barrier layer.