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(56) Documents Cited
1999 E-MRS Conf. Strasbourg June 1999, & App. Surf. Sci. 2000, vol 154-155, pp 35-39
J.App. Phys.,1999, vol 86, no 5, pp 2562-2570
Tech. Phys. Lett., 1998, vol 24, no 2, pp 124-126
App. Phys. Lett.,1982, vol 40, no 3, pp 258-260

(58) Field of Search
UK CL (Edition S) H1K KEAL KEAM KLHA KLHX KLXW
INT CL^7 H01L 33/00 , H05B 33/10
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(54) Abstract Title
Production of a thin film electroluminescent device

(57) To produce a thin film electroluminescent device of the kind comprising a substrate 1, conductor, dielectric layer 2 and phosphor layer 3, the phosphor layer is transiently laser annealed so as to induce an in-depth annealing effect therein without heating the phosphor/dielectric region interface above a temperature which induces a substantial modification in the distribution of electron interface states in the interface region. This method improves the luminosity of the device without softening the brightness-voltage characteristic. The phosphor layer may be raised to at least 1295°K but the interface region is not raised above 870°K. The annealing is preferably done by an excimer layer with a pulse duration of between 0.1ns and 500ns. A buffer layer may be incorporated in the device to act as a heat sink. The phosphor layer preferably comprises two or more allotropes of ZnS, the annealing inducing a solid state phase transition therebetween. Alternatively the phosphor layer may comprise SrS, Y_2O_3, YAG or ZnO. It may be doped with at least one transition metal or rare earth luminescent centres comprising Mn, Tb, Tm, TmF, Ce, Er, Eu or mixtures thereof.

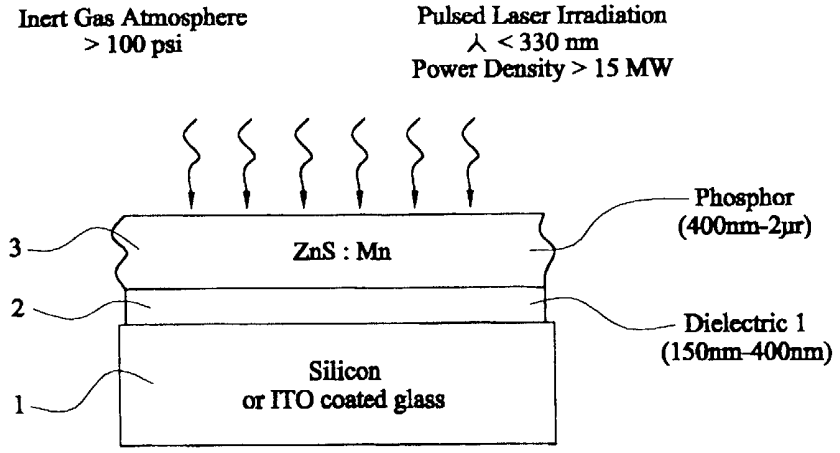

FIG. 2

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1995

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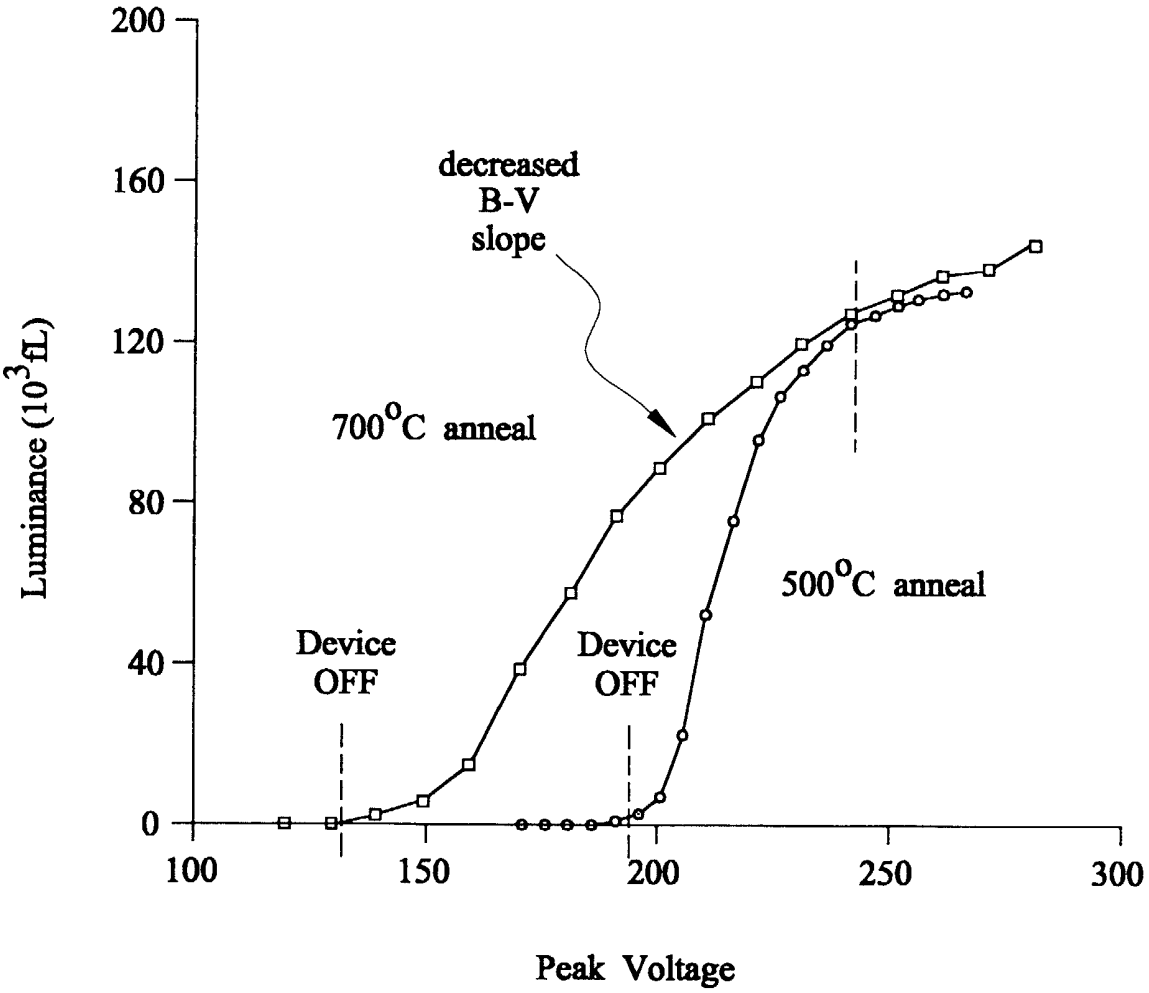
200
160
120
80
40
0
Luminance (10^3fL)
decreased
B-V
slope
700°C anneal
500°C anneal
Device
OFF
Device
OFF
100
150
200
250
300
Peak Voltage

FIG. 1

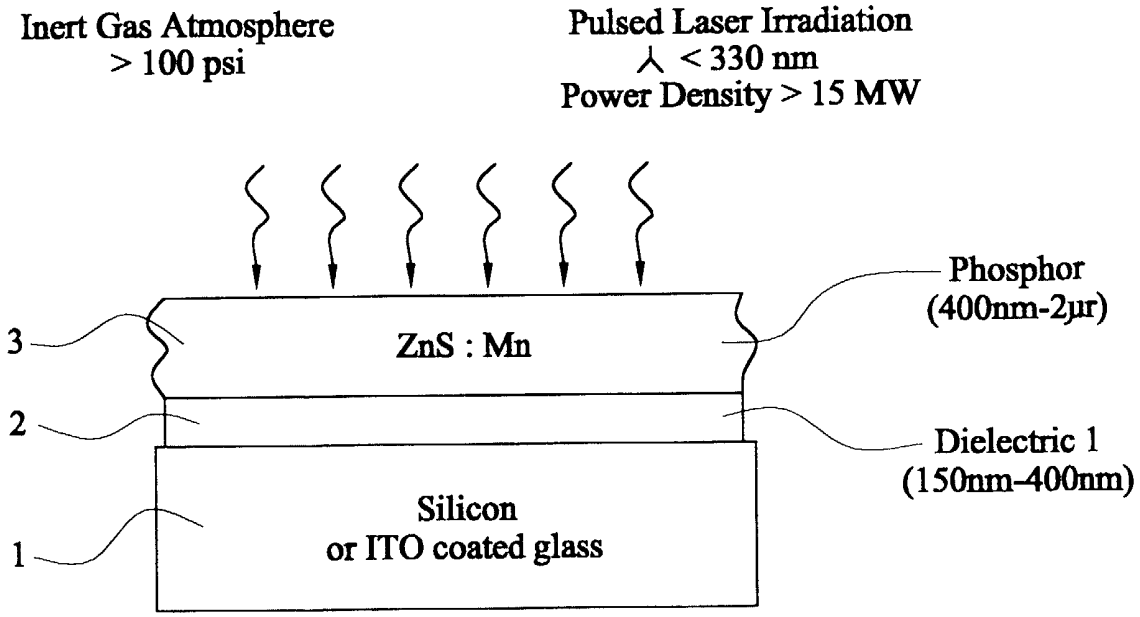
Inert Gas Atmosphere
> 100 psi
Pulsed Laser Irradiation
人 < 330 nm
Power Density > 15 MW
Phosphor
(400nm-2μr)
3
ZnS : Mn
2
Dielectric 1
(150nm-400nm)
Silicon
or ITO coated glass
1

FIG. 2

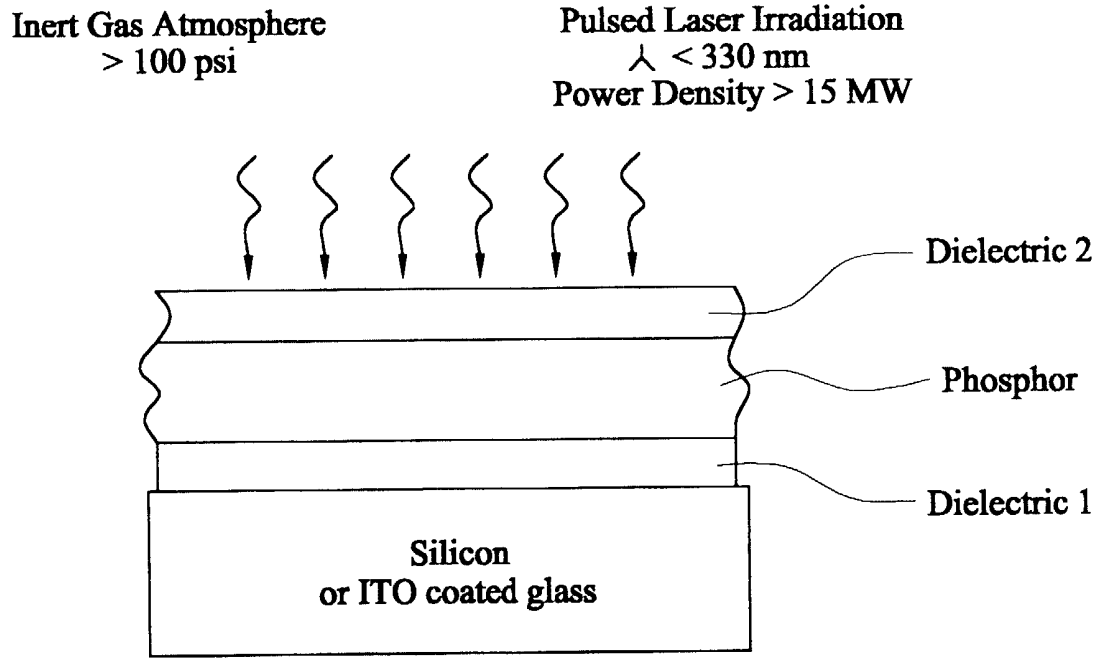
Inert Gas Atmosphere
> 100 psi
Pulsed Laser Irradiation
人 < 330 nm
Power Density > 15 MW
Dielectric 2
Phosphor
Dielectric 1
Silicon
or ITO coated glass

FIG. 3

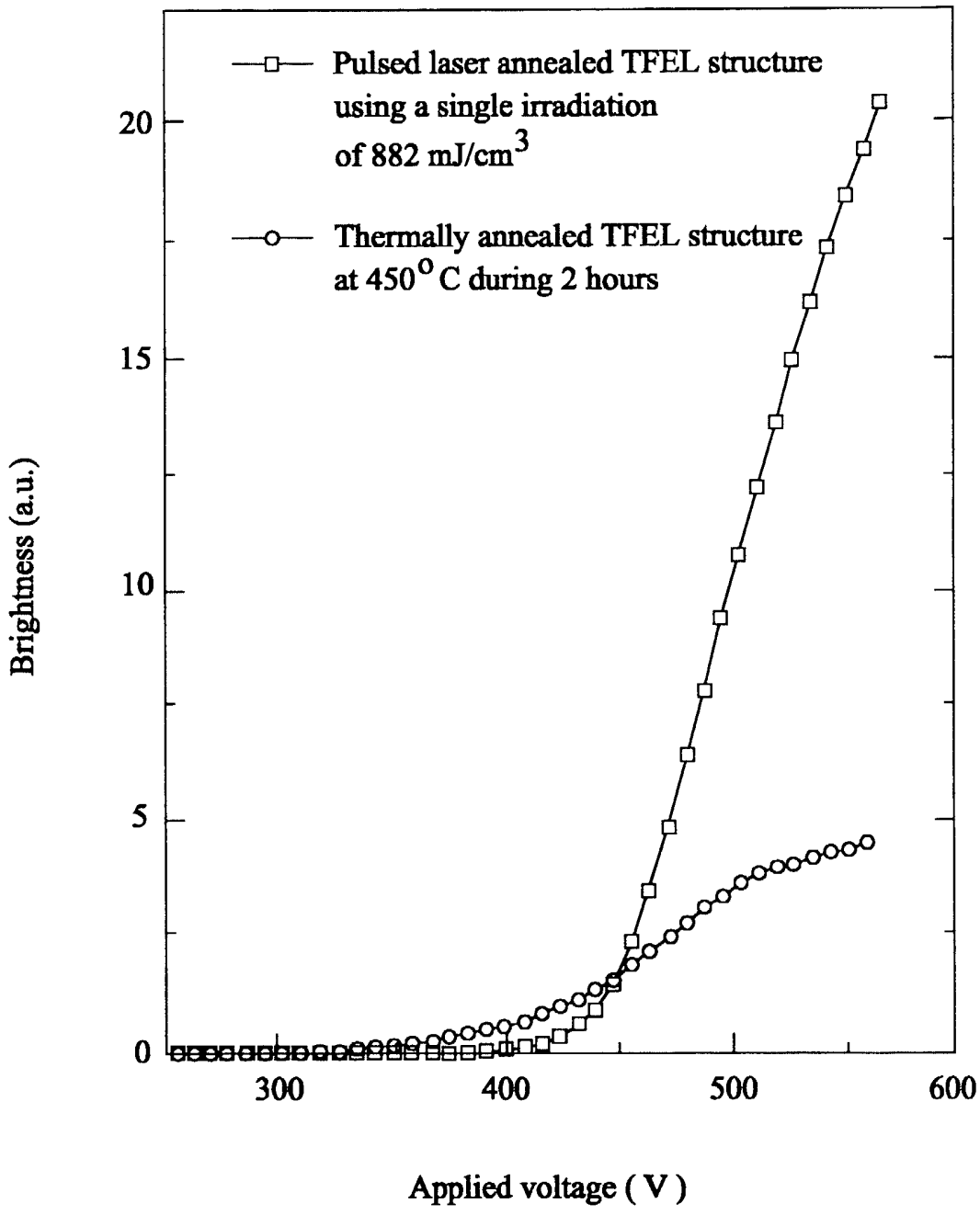
Pulsed laser annealed TFEL structure
using a single irradiation
of 882 mJ/cm3
Thermally annealed TFEL structure
at 450° C during 2 hours
Brightness (a.u.)
0
5
10
15
20
300
400
500
600
Applied voltage (V)

FIG. 4

A Method Of Production Of A Thin Film Electroluminescent Device

The present invention relates to a method of production of a thin film electroluminescent device and also such devices.

The basic thin film electroluminescent structure (TFEL) consists of a phosphor thin film sandwiched between two insulating dielectric layers. In its simplest form, the full device is completed by the deposition of conductors on the outer surfaces of both dielectrics.

Light is produced by such devices by the application of a suitable AC drive voltage across the dielectrics. The electroluminescent characteristics and performance of the TFEL device are governed by three distinct mechanisms - firstly the field emission of the charged carriers from trapped electron interface states at the phosphor/dielectric interface, secondly the acceleration of the charge carriers under the electric field, and finally energy to transfer of the latter to luminescent centres followed by their radiative decay. Highly efficient TFEL devices are recognised by a sharp turn on slope and high brightness.

Critical to the performance of any TFEL device is the post deposition annealing treatment for the phosphor layer which facilitates the effective incorporation of the luminescent centres within the host lattice and improves its crystalline structure. It is known that such post deposition annealing at high temperatures can improve the luminosity of the resulting device.

Conventional thermal annealing techniques rely on processing times long enough to allow solid state defusion processes to

occur. In one known technique the entire structure (i.e. the phosphor layer, the dielectric layers and the substrate) is heated. The annealing temperature is limited by either the melting temperature of the type of substrate used or by the induced modifications of the trapped electron interface states. For example, a typical TFEL device comprises of thin film of ZnS on a borosilicate glass. The ZnS has a melting temperature of 1820°C but the annealing temperature is limited to around 600°C as borosilicate glass softens around 570°C.

In the past, various approaches have been taken to treat the phosphor layer without damaging the commonly used glass substrate. One such process is disclosed in H S Reehal et al, Appl.Phys.Lett 40 (1982) 258, in which a nanosecond pulsed laser melting under high inert gas pressure diffuses and activates the pre-implanted Mn irons within the ZnS lattice. US4 442 136 discloses a similar method in which the ZnS lattice is melted under inert gas using a CW laser with high power density. Both of these approaches propose a substantial improvement in the TFEL device by generating a deep melt front within the ZnS lattice. However, whilst known annealing processes improve the brightness of the resulting devices they "soften" the brightness-voltage characteristics of these devices. This has the effect of broadening the voltage range over which the devices switch on. Electroluminescent devices which switch on over a narrow voltage range are preferred.

Accordingly, in the first aspect, the present invention provides a method of production of a thin film electroluminescent device comprising the steps of

providing a substrate;

providing a conductor on the substrate;

providing a dielectric layer on the conductor;

providing a phosphor layer on the dielectric layer so creating a phosphor/dielectric interface region, the phosphor/dielectric interface region comprising a plurality of electron interface states; and,

transiently laser annealing the phosphor layer so as to induce an in depth annealing effect in the phosphor layer without heating the phosphor/dielectric region above a temperature which induces a substantial modification in the distribution of the electron interface states.

The method according to the invention has the advantage that the resulting device has an improved luminosity without a softened brightness-voltage characteristic.

Preferably, the step of transiently laser annealing the phosphor layer produces a reduction in the slope of the brightness vs voltage characteristic of the resulting device of less than 10% as compared to an equivalent device annealed at 500 degrees Centigrade. This ensures that even after the annealing step the device can be switched on by a relatively narrow change in applied voltage.

The phosphor layer can comprise two or more allotropes of the phosphor; and the step of transiently laser annealing the phosphor layer induces a solid state phase transition between the allotropes of the phosphor layer.

Preferably the phosphor layer comprises ZnS. This has two stable allotropes (zinc blende and wurzite) which have a

phase transition at around 1295K which is well below the melting point of 2100K.

Preferably the phosphor layer comprises one of SrS or Y_2O_3.

The phosphor layer can be doped with at least one of transition metal or rare earth luminescent centres, preferably at least one of Mn, Tb, Tm, TmF, Ce, Er, Eu or mixtures thereof.

The step of transiently laser annealing the phosphor layer can raise the temperature of at least a portion of the phosphor layer to at least 1295 kelvin, but does not raise the temperature of the interface region above 870 kelvin. This ensures that whilst the phosphor layer is raised to a temperature sufficient to cause annealing, the interface region is not raised above a temperature at which the distribution of interface states is substantially modified.

The transient laser annealing can be by pulse laser, preferably by excimer laser, more preferably one of a KrF, XeCl or XeF laser. Pulse duration can be between 0.1 ns and 500 ns.

The method of production of a thin film electroluminescent device according to the invention can further comprise the step of providing a gaseous medium in contact with the phosphor layer during the annealing, the pressure of the inert gas preferably being greater than 100psi. This has the advantage that material dissociation at the surface of the device is reduced. Preferably the gas is inert, more preferably argon. The gas can be reactive, preferably $Ar:H_2S$.

Preferably the method can further comprise the step of providing a buffer layer underlying at least one of the

phosphor or dielectric layers. The buffer layer can be adapted to act as a heat sink. Preferably the buffer layer is a insulator or charge reservoir layer.

The present invention will now be described by way of example only, and not in any limitative sense, with reference to the accompanying drawings in which

Figure 1 shows the effect of a known annealing process on a thin film electroluminescent device;

Figures 2 and 3 show, in schematic form, laser annealing of a thin film electroluminescent device of a method according to the invention; and

Figure 4 shows the effect of the method of annealing according to the invention on a thin film electroluminescent device.

Shown in Figure 1 is the effect of a known annealing process on a thin film electroluminescent device. The device comprises a substrate, conductor, a dielectric layer on the conductor and a phosphor layer disclosed on the dielectric layer. The method of annealing comprises the step of heating the entire structure to a uniform temperature for a fixed hold time whilst annealing occurs in the phosphor layer. The structure is then cooled to room temperature. As can be seen from figure 1, increasing the annealing temperature has the effect of broadening the voltage range over which the resulting device switches on. This is because heating the phosphor and dielectric layers to such high temperatures alters the trapped electron states at the phosphor/dielectric layer interface. These trapped electrons states are important in determining the width of this voltage range. These trapped electron states are also important in

determining the brightness of the resulting device. Such a known annealing method has the effect of substantially modifying the distribution of trapped electron interface states and hence the brightness of the resulting devices.

Shown in Figure 2 is a cross sectional view of a portion of a thin film electroluminescent device. The device comprises substrate 1, a first dielectric layer 2 and a phosphor layer 3.

The substrate 1 comprises a silicon layer. The phosphor layer comprises ZnS is doped with Mn luminescent centres. The composition of the phosphor layer of this embodiment of the invention is ZnS:Mn (0.43wt%) which is one of the most efficient TFEL phosphors. The ZnS:Mn layer is approximately 800nm thick. The dielectric layer is comprised of Y_2O_3. This layer is approximately 300nm thick.

In a method according to the invention, a KrF excimer laser with a wavelength of 249nm is used to provide pulses of 20 ns duration with an energy density greater than 300 millijoules per centimetre squared (hence providing a delivered power density of > 15MW/cm^2). At this power density, the heat operated by the laser provides a surface temperature of > 1295 kelvin in the phosphor layer but does not raise the dielectric phosphor interface to a temperature greater than 870 kelvin. This induces an in-depth annealing effect in the phosphor layer in the form of a measurable phase transition in the predominantly cubic ZnS to the hexagonal phase which is the stable allotrope at high temperatures. This results in an increase in the hexagonal crystallites and an increase in the luminescence both by photo luminescence and by electroluminescence excitation. The resultant TFEL device exhibits a four fold improvement in electroluminescent brightness as shown in Figure 4. An important aspect of

Figure 4 is that the slope of the B-V characteristic remains sharp even after annealing. This can be contrasted with electroluminescent devices which have been annealed at temperatures in excess of 500 degrees Celsius by known annealing methods in which the B-V slope is reduced.

The method is applicable to all phosphor thin films requiring annealing for activation where it is critical that in depth melting or high temperature effects at the phosphor dielectric interface are minimised. The technique requires the use of a pulse laser radiating of a wave length suitable to provide high surface absorption in the phosphor thin film. Depending on the available beam area cross section the laser pulse can be applied to individual emitting areas via scanning. Alternatively, for larger beams the laser pulse can be applied to the entire substrate provided that the power density is above the transition threshold for the particular phosphor used (e.g. > 15 mw/cm for ZnS:Mn).

It is advantageous to perform the laser irradiation in a high pressure gas atmosphere (preferably > 100psi) to reduce dissociation effects eg ablation. The gas can be inert (preferably argon) or can contain reactive elements to enhance annealing such as H_2S, or S_2.

In a further embodiment of the invention (not shown) the electroluminescent device includes a buffer layer. This buffer layer underlies the phosphor layer (or possibly the dielectric layer). In use this buffer layer acts as a heat sink. Examples of suitable buffer layers include insulators or charge reservoirs such as ITO, SiO_2 and Y_2O_3.

In an alternate embodiment of the invention the substrate is of a size suitable for use in large area displays, typically greater than 100 mm.

In alternative embodiments of the invention the phosphor layer is doped with luminescent centres comprising transition metals or rare earths. Examples include TmF, Ce, Er, Eu or mixtures thereof.

In an alternative embodiment the phosphor layer comprises at least one of SrS, Y_2O_3, YAG and ZnO.

In an alternate embodiment the dielectric layer can further include $BaTiO_3$, SiON, Si_3N_4, SiO_2 and suitable combinations thereof.

In an alternate embodiment the pulse laser is an excimer laser, preferably one of Xef, XeCl and KrF.

In an alternate embodiment single or multiple irradiations can be used per single target area.

Shown in table 1 are results of x-ray characteristics determined for samples annealed by a known thermal method and also for samples laser annealed by a method according to the invention. The studied structure was a multilayer of ZnS:Mn (800nm)/Y_2O_3 (300nm) deposited on Si. $I_{111,ZnS}$ and $I_{222,Y2O3}$ are the integrated intensities of the diffraction lines corresponding to the cubic forms of ZnS:Mn (111) and Y_2O_3 (222) lines, respectively.
$I_{00.2,ZnS}$ is the integrated intensity of the ZnS (00.2) diffraction line belonging to the hexagonal wurzite form of ZnS. The hexagonal structure of ZnS only appears with laser processing suggesting that temperatures within the phosphor layer are higher than the transition temperature, i.e., around 1295 K. However, as evidence by the diffraction intensity of the insulator layer (I_{222},Y_2O_3), the temperature attained at the interface is <600°C. A study of the full width at half maximum of the diffraction peaks, dependent on

grain size, does not show significant changes implying that no substantial grain growth occurs. In turn, although surface melting might occur using laser power densities up to 48 MW/cm^2, the melting region remains at the surface of the phosphor layer.

		Thermal annealing temp. (°C)			P_d (MW/cm^2)	
		200	500	600	6	48
$I_{222,Y2O3}$	(a.u.)	599±2	1642±17	4320±36	1903±80	2394±89
$I_{111,ZnS}$	(a.u.)	20±4	54±4	648±13	1114±45	-
$I_{00.2,ZnS}$	(a.u.)	-	-	-	-	1383±50

Claims

1. A method of production of a thin film electroluminescent device comprising the steps of

providing a substrate;

providing a conductor on the substrate;

providing a dielectric layer on the conductor;

providing a phosphor layer on the dielectric layer so creating a phosphor/dielectric interface region, the phosphor/dielectric region interface comprising a plurality of electron interface states; and

transiently laser annealing the phosphor layer so as to induce an in depth annealing effect in the phosphor layer without heating the phosphor/dielectric region above a temperature which induces a substantial modification in the distribution of electron interface states.

2. A method of production of a thin film electroluminescent device as claimed in claim 1, wherein the step of transiently laser annealing the phosphor layer produces a reduction in the slope of the brightness versus voltage characteristic of the resulting device of less than 10% compared to an equivalent device annealed to 500 degrees Celsius.

3. A method of production of a thin film electroluminescent device as claimed in either of claims 1 or 2, wherein the phosphor layer comprises two or more allotropes of the phosphor; and

the step of transiently laser annealing the phosphor layer induces a solid state phase transition between the allotropes of the phosphor layer.

4. A method of production of a thin film electroluminescent device as claimed in claim 3, wherein the phosphor layer comprises ZnS.

5. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 3, wherein the phosphor layer comprises one of SrS, Y_2O_3, YAG or ZnO.

6. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 5, wherein the phosphor layer is doped with at least one of transition metal or rare earth luminescent centres, preferably at least one of Mn, Tb, Tm, TmF, Ce, Er, Eu or mixtures thereof.

7. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 6, wherein the step of transiently laser annealing the phosphor layer raises the temperature of at least a portion of the phosphor layer to at least 1295 kelvin, but does not raise the temperature of the interface region above 870 kelvin.

8. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 7, wherein the transient laser annealing is by a pulse laser, preferably an excimer laser, preferably one of a KrF, XeCl or XeF laser, the pulse duration preferably being between 0.1 ns and 500 ns.

9. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 8 further comprising the step of providing a gaseous medium in contact with the phosphor layer during the annealing, the pressure of the gaseous medium preferably being greater than 100psi.

10. A method of production of a thin film electroluminescent device as claimed in any one of claims 1 to 9, further comprising the step of providing a buffer layer underlying at least one of the phosphor or dielectric layers, the buffer layer being adapted to act as a heat sink.

11. A method of production of a thin film electroluminescent device as claimed in claim 10, wherein the buffer layer is an insulator or charge reservoir layer.

12. A method of production of a thin film electroluminescent device substantially as herein before described.

13. A method of production of a thin film electroluminescent device substantially as herein before described with reference to the drawings.

Application No: GB 0002231.9
Claims searched: all

Examiner: Martyn Dixon
Date of search: 19 November 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): H1K (KEAL,KEAM,KLHA,KLHX,KLXW)

Int Cl (Ed.7): H01L (33/00); H05B (33/10)

Other: Online: EPODOC,WPI,JAPIO,INSPEC,IEL

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	1999 E-MRS Spring Conference, Strasbourg, June 1999, Symposium A on Photo-Excited Processes, Diagnostics and Applications, & Applied Surface Science, 2000, vol 154-155, Mastio *et al*, "Ablation study on paulse KrF laser annealed electroluminescent ZnS:Mn/Y_2O_3 multilayers deposited on Si", pages 35-39	1,6-9
A	Journal of Applied Physics, 1999, vol 86, no 5, Mastio *et al*, "The effects of KrF pulsed laser and thermal annealing on the crystallinity and surface morphology of radiofrequency magnetron sputtered ZnS:Mn thin films deposited on Si", pages 2562-2570	
A	Technical Physics Letters, 1998, vol 24, no 2, Kononets, "Enhancement of the characteristics of thin-film electroluminescent structures based on ZnS:Mn films after low-power laser irradiation", pages 124-126	
A	Applied Physics Letters, 1982, vol 40, no 3, Reehal *et al*, "Pulsed XeCl laser annealing of ZnS:Mn thin films", pages 258-260	

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