(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 648 042 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
19.04.2006 Bulletin 2006/16

(51) Int Cl.:
H01L 51/40 *(2006.01)* ***H01L 51/50*** *(2006.01)*

(21) Application number: **04023945.1**

(22) Date of filing: **07.10.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL HR LT LV MK

(71) Applicant: **Novaled GmbH**
01307 Dresden (DE)

(72) Inventors:
- **Werner, Ansgar**
  01277 Dresden (DE)
- **Romainczyk, Tilmann**
  01099 Dresden (DE)

(74) Representative: **Bittner, Thomas L.**
Forrester & Boehmert
Pettenkoferstrasse 20-22
80336 München (DE)

Remarks:
Amended claims in accordance with Rule 86 (2) EPC.

(54) A method for doping a semiconductor material with cesium

(57) The invention relates to a method for doping a semiconductor material with Cesium, wherein said semiconductor material is exposed to a cesium vapor. Said Cesium vapor is provided by Cesium sublimation from a Cesium alloy. There is also provided an organic light emitting diode comprising at least one layer of a Cesium doped organic semiconductor material, wherein said at least one layer of said Cesium doped organic semiconductor material is doped with Cesium provided by Cesium evaporation of Cesium from a Cesium alloy. The Cesium vapor is preferably provided by Cesium sublimation from a standard organic material deposition evaporator.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The invention relates to a method for electrical doping a semiconductor material with Cesium, and an organic light emitting diode (OLED) comprising at least one layer of a Cesium doped semiconductor material. Electrical doping a semiconductor material means the admixture of dopant molecules to the semiconductor materials to increase the conductivity of the semiconductor material by increasing the intrinsic charge carrier density on the semiconductor material.

Background of the invention

[0002] Such doped semiconductor layers are for example used in organic light emitting diodes. Doping of electron transport layers (ETL) in organic light emitting diodes using alkali metals is an established technique to improve the power efficiency of such devices. Due to the unavailability of sufficiently strong molecular donors, alkali metals are used as donor atoms. Among the alkali metals, Cesium (Cs) is frequently used because it gives the highest stability of OLED with such doped ETL. Organic semiconductors are referred to as electron transport materials if whether their electron mobility is higher than their hole mobility, or their electron mobility is bigger than 1E-6 cm2/Vs (in the relevant field range of around 1-100E5V/cm). The ETL materials needs to be stable against reduction to support electron current over a long time. The energetic position of the lowest unoccupied molecular level (LUMO) is in the range from 2.4eV to 3.8eV, preferably 2.4 to 3eV.

[0003] Currently, the only possibility to provide Cs vapor for doping purposes is the use of so called getter sources provided by S.A.E.S. getters. In this sources, $CsCrO_4$ or $CsMoO_4$ salts are decomposed by thermolysis and the released vapor guided through getter materials which removes the oxygen from the gas phase. After passing the getter, pure Cs vapor is released.

[0004] There are several drawbacks combined with this type of sources. The sources need very high operating temperatures to carry out thermolysis. The container of the source achieves temperatures above 400°C during operation, while the content is heated even more. This causes extra effort for cooling of the vacuum chamber. Due to strong gas adsorption at the getter material, severe degassing is observed during heat up, especially when the source was exposed to air beforehand. It takes a long time (ten min) until the Cs dispenser releases Cs vapor. Another ten minutes has to pass before the Cs evaporation rate is sufficiently stable. No rate is observed at quartz microbalances placed over the dispenser even when the former is water cooled. This is a major obstacle to process control. Checks for the proper operation of the source have to be carried out on a regular basis, which reduces the throughput of the vacuum chamber and adds to maintenance time and effort. Due to the complicated arrangement of the various components of such a source, it geometry flexibility is restricted, resulting in space demanding set-ups and limited evaporation characteristics. Finally, at least for $CsCrO_4$, health and environmental risks are immanent due to the high toxicity of that compound.

Summary of the invention

[0005] It is the object of the invention to provide a method for electrical doping a semiconductor material with Cesium, where electrical doping can be performed in a more simple fashion with improved process control.

[0006] According to one aspect of the invention a method for electrical doping a semiconductor material with Cesium is provided, wherein said semiconductor material is exposed to a Cesium vapor. Said Cesium vapor is provided by Cesium sublimation from a Cesium alloy.

[0007] According to another aspect of the invention an organic light emitting diode is provided, wherein said organic light emitting diode comprising at least one layer of a Cesium doped organic semiconductor material and said at least one layer of said Cesium doped organic semiconductor material being doped with Cesium provided by Cesium evaporation of Cesium from a Cesium alloy.

[0008] The invention provides the advantage that Cesium sublimation for electrical doping a semiconductor material is easier to control, since controlling and measuring of the sublimation rate is improved. Overall controlling of the process of electrical doping is more reliable.

[0009] Advantageous developments of the invention are disclosed in dependent claims.

Description of preferred embodiments of the invention

[0010] Following the invention will be described in further detail, by way of example, with reference to different embodiments.

[0011] A method for doping a semiconductor material with Cesium (Cs) is described, wherein said semiconductor material is exposed to a cesium vapor. Said Cesium vapor is provided by Cesium sublimation from a Cesium alloy. Preferably GaCs alloys offer a possibility to provide Cs vapor. Here, Cs is released from the surface of the alloy at moderate temperatures. Simultaneously, further Cs diffuses through the core to the surface. The evaporation proceeds with a constant sublimation rate for a given temperature until finally the Cs content is used up. Under appropriate conditions, a thin shell of pure Ga is produced covering the air-sensitive GaCs core. In that instance, the GaCs pieces can be handled in air at least for several tens of minutes without degradation, means a negative effect on the doping capability of the Cs vapor..

[0012] The cesium evaporation takes place already at moderate temperatures around 300°C. It is possible to measure a Cs rate on a water cooled quartz microbalance. The source operation is quick. Stable Cs rate are provided by temperature control. Standard evaporators for organic materials can be used to evaporate the GaCs alloy.

[0013] In an embodiment a Bathophenanthroline (BPhen) layer shows an increase in conductivity, when it is exposed to vapor released by the GaCs alloy. BPhen is a well known electron transport material in the OLED field and can be easily doped with Cs.

[0014] In the course of the experiments, it was noted that the quartz microbalance (QMB1) usually used to monitor the evaporation of molecular compounds display a stable evaporation rate during the operation of the GaCs alloy evaporator. When the evaporation temperature is operated at a stable temperature, a constant rate is observed over time. This is in contrast to the observation for S.A.E.S. Cs dispensers, where no stable rates were observed.

[0015] Calibration of the evaporation was performed. For this purpose, a second quartz microbalance (QMB2) is placed at the position of the sample. By comparison of the rates measured by QMB2 with QMB1, the geometric tooling factor can be determined. It was observed that QMB2 displayed a rate decreasing with time while the evaporator was operated at a stable temperature and QMB1 showed a stable rate. The reason for the differing behavior is most likely the fact that QMB 1 is water cooled, while the uncooled QMB2 may heat up during operation. This could reduce the sticking coefficient of the Cs atoms impinging on the quartz surface. Calibration of the source was than attempted using surface analysis of a Cs doped organic film using X-ray photoelectron spectroscopy (XPS).

[0016] In a further embodiment, two samples of Cs doped films were prepared by co-evaporation on Au substrates. As matrices, metal complexes have been employed. The XPS signal of the corresponding metal atoms gives further information on the stoichiometry of the film. Both films have a nominal doping concentration of 1.8 : 1 (ratio Cs to matrix material), as determined by the measured evaporation rates and assuming the tooling factor for the Cs evaporator to be similar to values found earlier for molecular dopants.

[0017] The films were transferred to the XPS analysis chamber through air. Consequently, a sputtering step has been carried out to remove over-layers of adsorbed gas. XPS spectra were recorded for Al Kα irradiation (1486.61eV). In Fig. 1 to 3 representative peaks XPS for a Cs:Ir(ppy)$_3$ sample are depicted. Ir(ppy)$_3$ (Tris(2-phenylpyridine) iridium) is not a dopable electron transport matrix material for OLEDs but serves here as a reference molecule which Iridium central atom can be easily detected by XPS. No XPS signal from Ga was detected. After background subtraction, the areas of the various peaks were determined. These areas need to be corrected for the elemental sensitivity factors specific for the spectrometer and the escape depth variation with the kinetic energy of the photoelectrons. Table 1 summarizes the determined stoichiometry (metal and carbon peaks have been combined using the known molecular structure of the matrix material). Also given in table 1 is the stoichiometry of a Cs doped BPhen layer typically used in OLEDs.

Table 1

	Cs:Ir(ppy)$_3$	Cs:Alq	Cs:BPhen
Cs	3.2 (1.8 exp.)	3.1 (1.8 exp)	1
Matrixmaterial	1	1	8.1

[0018] In a still further embodiment doping of various matrices has been carried out using a Ga$_7$Cs$_{11}$ alloy. The compound was subjected to heating to 420°C before use in order to create a protective Ga shell. A total of 15 doped samples have been prepared with one crucible filling (approx. 0.1g equivalent of pure Cs). Still, no sign of exhaustion has occurred. The sublimation temperature for Cs is around 300°C. This corresponds to an equivalent of about 100nm of pure Cs in the doped films (source — sample distance approx. 25cm). Additionally, further Cs is wasted before and after the experiment. It was estimated that the 0.1g equivalent of pure Cs should be sufficient for 3000nm total layer thickness of Cs. Table 2 shows examples for the doping process according to this embodiment.

Table 2

	Nominal doping concentration Cs:BPhen	Corrected doping concentration Cs:BPhen	Conductivity (S/cm)
Cs: BPhen prepared using GaCs alloy	1:9	1:5	6.7e-5

Table continued

	Nominal doping concentration Cs:BPhen	Corrected doping concentration Cs:BPhen	Conductivity (S/cm)
	1:7.5	1:4	7.6e-5
	1:18	1:10	1.5e-6
Cs: BPhen prepared using S.A.E.S. getter		1:8	5e-5
Nominal doping concentrations determined from QMB readout, corrected values include non-unity sticking coefficient of Cs			

[0019] Electrical doping as described above can be advantageously performed by means of a standard evaporator or crucible as used for organic material deposition in vacuum. One preferred evaporator design is of the so called Knudsen type which comprises an electrical heated cylindrical crucible usually used as a point source where a large distance between crucible and the substance to be doped is provided. The Knudsen type evaporator can be extended linearly to provide a linear source.

[0020] An alternative linear source comprises a linear evaporator head with holes. The head is connected to an independently heated volume via a heated tube system. Material released from the crucible inside the heated volume is transported through the tube system to the linear evaporator head and released through the holes towards the substance to be doped. In such evaporator the Cesium alloy can be handled as a standard organic material. The crucible can be heated to about 420°C or less, preferably to about 300°C or less to release Cesium vapor. The heated tube system and the linear head can be operated at temperatures above the crucible temperature (up to 50°C) until down to 50°C.

[0021] The temperature of the tube system can be kept at a lower temperature than the sublimation temperature in the crucible volume to avoid chemical reactions. Thus less energy is consumed during electrical doping process.

[0022] The features disclosed in this specification, claims and/or the figures may be material for the realization of the invention in its various embodiments, taken in isolation or in various combinations thereof.

Claims

1. A method for electrical doping a semiconductor material with Cesium, wherein said semiconductor material is exposed to a Cesium vapor, **characterized in that** said Cesium vapor is provided by Cesium sublimation from a Cesium alloy.

2. The method as claimed in claim 1, wherein said Cesium vapor is provided by Cesium sublimation from a Gallium Cesium alloy.

3. The method as claimed in claim 2, wherein said Cesium vapor is provided by Cesium sublimation from a Ga_7Cs_{11} alloy

4. The method as claimed in one of the preceding claims, wherein said semiconductor material is provided as a thin film material.

5. The method as claimed in one of the preceding claims, wherein said Cesium sublimation is performed in an evaporator at a sublimation temperature of about 420°C or less, preferably at a sublimation temperature of about 300°C or less.

6. The method as claimed in one of the preceding claims, wherein said Cesium sublimation is monitored by a quartz microbalance.

7. The method as claimed in claim 6, wherein said quartz microbalance is cooled by water.

8. The method as claimed in one of the preceding claims, wherein said Cesium alloy is provided as a solid material, and said solid material is preheated for generating a protective shell.

9. The method as claimed in one of the preceding claims, wherein said semiconductor material is an organic material.

10. The method as claimed in one of the preceding claims, wherein said semiconductor material is an organic electron transport material.

11. The method as claimed in one of the preceding claims, wherein said Cesium vapor is provided by Cesium sublimation from a standard organic material deposition evaporator.

12. The method as claimed in claim 11, wherein said standard organic material deposition evaporator is a Knudsen type crucible.

13. The method as claimed in one of the claims 1 to 11, wherein said standard organic material deposition evaporator is a linear source type.

14. The method as claimed in one of the claims 1 to 11, wherein said standard organic material deposition evaporator is an evaporator with a linear head connected to a crucible volume by a tube system.

15. The method as claimed in claim 14, wherein a temperature of said tube system of said standard organic material deposition evaporator is controlled to be below a temperature in said crucible volume.

16. Organic light emitting diode comprising at least one layer of a Cesium doped organic semiconductor material generated by a method according to one of the claims 1 to 15, wherein said at least one layer of said Cesium doped organic semiconductor material is doped with Cesium provided by Cesium evaporation of Cesium from a Cesium alloy.

Amended claims in accordance with Rule 86(2) EPC.

1. A method for electrical doping a semiconductor material with Cesium, wherein said semiconductor material is exposed to a Cesium vapor, **characterized in that** said Cesium vapor is provided by Cesium sublimation from a Gallium Cesium alloy.

2. The method as claimed in claim 1, wherein said Cesium vapor is provided by Cesium sublimation from a Ga_7Cs_{11} alloy.

3. The method as claimed in one of the preceding claims, wherein said semiconductor material is provided as a thin film material.

4. The method as claimed in one of the preceding claims, wherein said Cesium sublimation is performed in an evaporator at a sublimation temperature of about 420°C or less, preferably at a sublimation temperature of about 300°C or less.

5. The method as claimed in one of the preceding claims, wherein said Cesium sublimation is monitored by a quartz microbalance.

6. The method as claimed in claim 5, wherein said quartz microbalance is cooled by water.

7. The method as claimed in one of the preceding claims, wherein said Cesium alloy is provided as a solid material, and said solid material is preheated for generating a protective shell.

8. The method as claimed in one of the preceding claims, wherein said semiconductor material is an organic material.

9. The method as claimed in one of the preceding claims, wherein said semiconductor material is an organic electron transport material.

10. The method as claimed in one of the preceding claims, wherein said Cesium vapor is provided by Cesium sublimation from a standard organic material deposition evaporator.

11. The method as claimed in claim 10, wherein said standard organic material deposition evaporator is a Knudsen type crucible.

12. The method as claimed in claim 10, wherein said standard organic material deposition evaporator is a linear source type.

13. The method as claimed in claim 10, wherein said standard organic material deposition evaporator is an evaporator with a linear head connected to a crucible volume by a tube system.

14. The method as claimed in claim 13, wherein a temperature of said tube system of said standard organic material deposition evaporator is controlled to be below a temperature in said crucible volume.

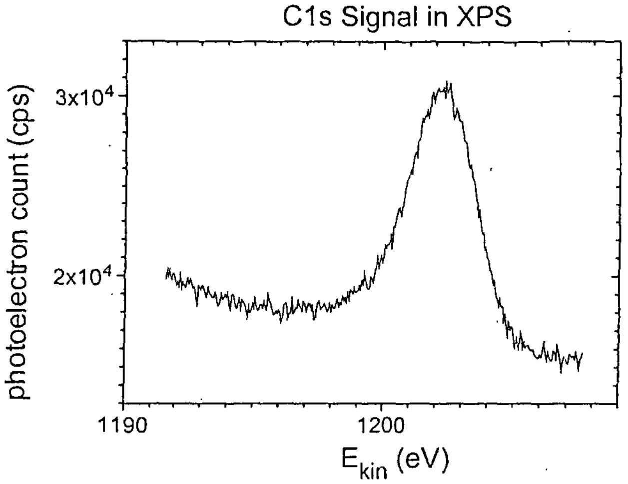

Fig. 1

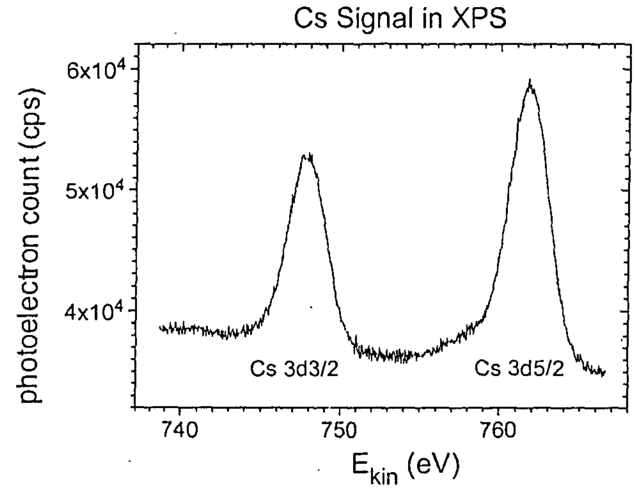

Fig. 2

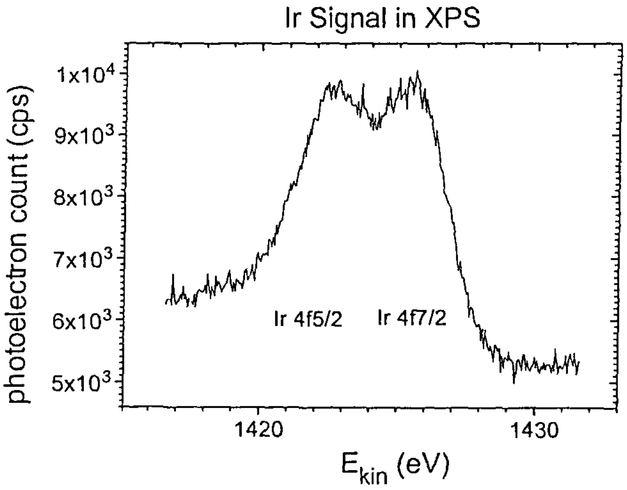

Fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 02 3945

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 02/093664 A (SAES GETTERS S.P.A; BOFFITO, CLAUDIO; TOIA, LUCA; CATTANEO, LORENA) 21 November 2002 (2002-11-21) * page 1, lines 6,9,26-30 * * page 2, lines 1-15,24-26 * * page 3, lines 12-17 * * page 8 - page 9, lines 1-9 *	1,4,6,7, 9,11-16	H01L51/40 H01L51/20
Y		10	
A		2,3,5,8	

X	DE 102 61 609 A1 (TECHNISCHE UNIVERSITAET DRESDEN) 8 July 2004 (2004-07-08) * page 6, paragraph 36 *	16	
Y		10	

X	EP 1 365 633 A (NEC CORPORATION) 26 November 2003 (2003-11-26) * page 4, paragraphs 23,24 * * pages 22,23, paragraphs 79,82 *	16	
A		1-15	
	-----		TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	GAO Y ET AL: "Cs doping and energy level shift in CuPc" CHEMICAL PHYSICS LETTERS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 380, no. 3-4, 21 October 2003 (2003-10-21), pages 451-455, XP004628152 ISSN: 0009-2614 * page 452, right-hand column *	1-16	H01L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	11 May 2005	Faou, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
&. : member of the same patent family, corresponding document

2

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 02 3945

11-05-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02093664 A	21-11-2002	IT MI20010995 A1	15-11-2002
		CA 2430941 A1	21-11-2002
		CN 1531839 A	22-09-2004
		EP 1419542 A2	19-05-2004
		WO 02093664 A2	21-11-2002
		JP 2004532932 T	28-10-2004
		US 2004001916 A1	01-01-2004
		US 2004206205 A1	21-10-2004
DE 10261609 A1	08-07-2004	AU 2003298073 A1	14-07-2004
		AU 2003303088 A1	14-07-2004
		WO 2004057686 A2	08-07-2004
		WO 2004057687 A2	08-07-2004
EP 1365633 A	26-11-2003	JP 2002198181 A	12-07-2002
		JP 2002198180 A	12-07-2002
		EP 1365633 A1	26-11-2003
		US 2004051097 A1	18-03-2004
		WO 02052905 A1	04-07-2002

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

专利名称(译)	一种用铯掺杂半导体材料的方法		
公开(公告)号	EP1648042A1	公开(公告)日	2006-04-19
申请号	EP2004023945	申请日	2004-10-07
[标]申请(专利权)人(译)	诺瓦莱德公开股份有限公司		
申请(专利权)人(译)	Novaled公司GMBH		
当前申请(专利权)人(译)	Novaled公司AG		
[标]发明人	WERNER ANSGAR ROMAINCZYK TILMANN		
发明人	WERNER, ANSGAR ROMAINCZYK, TILMANN		
IPC分类号	H01L51/40 H01L51/50 H01L51/56		
CPC分类号	H01L51/5052		
其他公开文献	EP1648042B1		
外部链接	Espacenet		

摘要(译)

本发明涉及一种用铯掺杂半导体材料的方法，其中所述半导体材料暴露于铯蒸气。所述铯蒸气由铯合金的铯升华提供。还提供了一种有机发光二极管，其包括至少一层铯掺杂的有机半导体材料，其中所述至少一层所述铯掺杂的有机半导体材料掺杂有铯，所述铯由铯从铯合金中蒸发铯而提供。铯蒸气优选通过铯升华从标准有机材料沉积蒸发器提供。

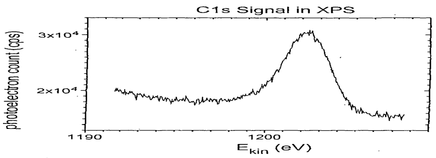

Fig. 1

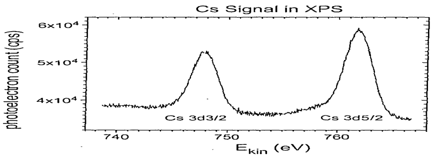

Fig. 2

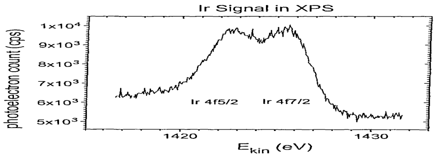

Fig. 3