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

Verfahren zur Dotierung von einem Halbleitermaterial mit Cäsium

Méthode de dopage d'un matériau semiconducteur avec du césium

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EP-A- 1 365 633 **WO-A-02/093664**
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- **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**

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Description

5 **[0001]** The invention relates to a method for electrical doping an organic semiconductor material with Cesium . Electrical doping an organic 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

10 **[0002]** Such doped organic 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
15 electron mobility is higher than their hole mobility, or their electron mobility is bigger than $1E-6 \text{ cm}^2/\text{Vs}$ (in the relevant field range of around $1-100E5\text{V}/\text{cm}$). 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.

20 **[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.

25 **[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
30 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.

35 **[0005]** Document WO 02/093664 A2 discloses a Cesium dispenser and a process for the use thereof. Due to its high reactivity to atmospheric gases and moisture, Cesium is not usually used as pure metal, but rather in the form of its compounds stable to air at room temperature. Some Cesium compounds release the metal by simple heating. Among these compounds, alloys with Silicon or Germanium may be cited. Such alloys are described for example in the document EP-A-360317 and the document US 5,066,888. However, it is stated that these compounds have no practical application at industrial level.

Summary of the invention

40 **[0006]** It is the object of the invention to provide a method for electrical doping an organic semiconductor material with Cesium, where electrical doping can be performed in a more simple fashion with improved process control.

45 **[0007]** According to one aspect of the invention a method for electrical doping an organic semiconductor material with Cesium is provided, wherein said organic semiconductor material is exposed to a Cesium vapor. Said Cesium vapor is provided by Cesium sublimation from a Gallium Cesium alloy.

50 **[0008]** The invention provides the advantage that Cesium sublimation for electrical doping an organic semi-conductor 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

55 **[0010]** Following the invention will be described in further detail, by way of example, with reference to different embodiments.

[0011] A method for doping an organic 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 example 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 displayed 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 example 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 K α irradiation (1486.61eV). XPS has been carried out for a Cs:Ir(ppy)₃ sample. 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 Ga₇Cs₁₁ 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)
5 Cs: BPhen prepared using GaCs alloy	1:9	1:5	6.7e-5
	1:7.5	1:4	7.6e-5
	1:18	1:10	1.5e-6
10 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			

15 **[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.

20 **[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.

25 **[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.

30 Claims

- 35 1. A method for electrical doping an organic semiconductor material with Cesium, wherein said organic semiconductor material is exposed to a Cesium vapor, **characterized in that** said Cesium vapor is provided by Cesium sublimation from a Gallium Cesium alloy.
- 40 2. The method as claimed in claim 1, wherein said Cesium vapor is provided by Cesium sublimation from a Ga₇Cs₁₁ alloy.
- 45 3. The method as claimed in one of the preceding claims, wherein said semiconductor material is provided as a thin film material.
- 50 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.
- 55 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 organic semiconductor material is an organic electron transport material.
9. 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.

10. The method as claimed in claim 9, wherein said standard organic material deposition evaporator is a Knudsen type crucible.

5 11. The method as claimed in claim 9, wherein said standard organic material deposition evaporator is a linear source type.

12. The method as claimed in claim 9, wherein said standard organic material deposition evaporator is an evaporator with a linear head connected to a crucible volume by a tube system.

10 13. The method as claimed in claim 12, 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.

Patentansprüche

15 1. Verfahren zum elektrischen Dotieren eines organischen Halbleitermaterials mit Cäsium, bei dem das organische Halbleitermaterial einem Cäsiumdampf ausgesetzt ist, **dadurch gekennzeichnet, daß** der Cäsiumdampf mittels Sublimation von Cäsium aus einer Gallium-Cäsium-Legierung bereitgestellt wird.

20 2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** der Cäsiumdampf mittels Sublimation von Cäsium aus einer Ga₇Cs₁₁-Legierung bereitgestellt wird.

25 3. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** das Halbleitermaterial als ein Dünnschichtmaterial bereitgestellt wird.

4. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** die Sublimation von Cäsium in einem Verdampfer bei einer Sublimationstemperatur von ungefähr 420°C oder weniger, vorzugsweise bei einer Sublimationstemperatur von ungefähr 300°C oder weniger durchgeführt wird.

30 5. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** die Sublimation von Cäsium mittels einer Quarzwaage überwacht wird.

6. Verfahren nach Anspruch 5, **dadurch gekennzeichnet, daß** die Quarzwaage mittels Wasser gekühlt wird.

35 7. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** die Cäsiumlegierung als ein festes Material bereitgestellt wird, wobei das feste Material vorerhitzt ist, um eine schützende Hülle zu erzeugen.

8. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** das organische Halbleitermaterial ein organisches Elektronentransportmaterial ist.

40 9. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, daß** der Cäsiumdampf mittels Sublimation von Cäsium von einem Standardverdampfer für organisches Material bereitgestellt wird.

45 10. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, daß** der Standardverdampfer für organisches Material ein Tiegel vom Typ Knudsen ist.

11. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, daß** der Standardverdampfer für organisches Material vom Typ lineare Quelle ist.

50 12. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, daß** der Standardverdampfer für organisches Material ein Verdampfer mit einem linearen Kopf ist, welcher mit einem Tiegelvolumen mittels eines Rohrsystems verbunden ist.

55 13. Verfahren nach Anspruch 12, **dadurch gekennzeichnet, daß** eine Temperatur des Rohrsystems des Standardverdampfers für organisches Material gesteuert wird, niedriger als eine Temperatur in dem Tiegelvolumen zu sein.

Revendications

- 5
1. Méthode pour le dopage électrique d'un matériau semi-conducteur organique avec du Césium, dans laquelle ledit matériau semi-conducteur organique est exposé à une vapeur de césium, **caractérisée en ce que** ladite vapeur de césium est fournie par sublimation de Césium à partir d'un alliage Gallium Césium.
 2. Méthode selon la revendication 1, dans laquelle ladite vapeur de césium est fournie par sublimation de Césium à partir d'un alliage Ga_7Cs_{11} .
 - 10 3. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ledit matériau semi-conducteur est fourni sous forme d'un matériau en film mince.
 4. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ladite sublimation du césium est réalisée dans un évaporateur à une température de sublimation d'environ 420 °C ou moins, de préférence à une température de sublimation d'environ 300 °C ou moins.
 - 15 5. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ladite sublimation du césium est suivie par une microbalance à quartz.
 - 20 6. Méthode selon la revendication 5, dans laquelle ladite microbalance à quartz est refroidie à l'eau.
 7. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ledit alliage de Césium est fourni sous forme d'un matériau solide, et ledit matériau solide est préchauffé pour générer une enveloppe protectrice.
 - 25 8. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ledit matériau semi-conducteur organique est un matériau organique transporteur d'électrons.
 9. Méthode selon l'une quelconque des revendications précédentes, dans laquelle ladite vapeur de Césium est fournie par sublimation du Césium à partir d'un évaporateur pour dépôt de matériaux organiques standard.
 - 30 10. Méthode selon la revendication 9, dans laquelle ledit évaporateur pour dépôt de matériaux organiques standard est un creuset de type Knudsen.
 11. Méthode selon la revendication 9, dans laquelle ledit évaporateur pour dépôt de matériaux organiques standard est de type source linéaire.
 - 35 12. Méthode selon la revendication 9, dans laquelle ledit évaporateur pour dépôt de matériaux organiques standard est un évaporateur à tête linéaire connectée à la cavité d'un creuset par un système de tubes.
 - 40 13. Méthode selon la revendication 12, dans laquelle une température dudit système de tubes dudit évaporateur pour dépôt de matériaux organiques standard est contrôlée de manière à être inférieure à une température dans la cavité dudit creuset.
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专利名称(译)	一种用铯掺杂半导体材料的方法		
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[标]申请(专利权)人(译)	诺瓦莱德公开股份有限公司		
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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。

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