United States Patent	12383879
Kind Code	B2
Date of Patent	August 12, 2025
Inventor(s)	Sun; Niefeng et al.

Semiconductor phosphide injection synthesis system and control method

Abstract

A semiconductor phosphide injection synthesis system and a control method are provided, which belong to the technical field of preparation of semiconductor phosphides. The semiconductor phosphide injection synthesis system includes a furnace body, a shielding carrier box arranged above the furnace body by virtue of a lifting mechanism, a phosphorus source carrier arranged in the shielding carrier box, an injection pipe arranged below the phosphorus source carrier, and a crucible arranged at an inner bottom of the furnace body in a matched manner. The phosphorus source carrier includes a phosphorus source carrier main body, a phosphorus source carrier upper cover, a heating element base arranged at an inner bottom of the phosphorus source carrier main body, and a heating element arranged on the heating element base; a heat insulation layer is wrapped on an outer wall of the phosphorus source carrier; and an induction coil is arranged between the heat insulation layer and an inner wall of the shielding carrier box. By improving a device and method, the system stability can be improved, and an entire synthesis system achieves quantitative synthesis, which lowers the risk of explosion of the phosphorus source carrier.

Inventors:	**Sun; Niefeng (Hebei, CN), Wang; Shujie (Hebei, CN), Liu; Huisheng (Hebei, CN), Sun; Tongnian (Hebei, CN)**
Applicant:	**THE 13TH RESEARCH INSTITUTE OF CHINA ELECTRONICS TECHNOLOGY GROUP CORPORATION** (Hebei, CN)
Family ID:	**1000008751236**
Assignee:	**THE 13TH RESEARCH INSTITUTE OF CHINA ELECTRONICS TECHNOLOGY GROUP CORPORATION (Shijiazhuang, CN)**
Appl. No.:	**17/797081**
Filed (or PCT Filed):	**July 05, 2021**
PCT No.:	**PCT/CN2021/104407**

PCT Pub. No.: **WO2022/134527**

PCT Pub. Date: June 30, 2022

Prior Publication Data

Document Identifier	Publication Date
US 20230049408 A1	Feb. 16, 2023

Foreign Application Priority Data

CN	202011543426.3	Dec. 23, 2020
CN	202023142510.2	Dec. 23, 2020

Publication Classification

Int. Cl.: **B01J10/00** (20060101); **B01J6/00** (20060101); **C01B25/08** (20060101); **G01K7/02** (20210101)

U.S. Cl.:

CPC **B01J10/005** (20130101); **B01J6/007** (20130101); **C01B25/087** (20130101); **G01K7/02** (20130101); C01P2006/40 (20130101)

Field of Classification Search

CPC: B01J (6/00); B01J (6/007); B01J (10/005); C01B (25/087); C30B (11/002); C30B (11/003); C30B (11/007)

References Cited

U.S. PATENT DOCUMENTS

Patent No.	Issued Date	Patentee Name	U.S. Cl.	CPC
3933435	12/1975	Menashi	432/262	C30B 29/44

Primary Examiner: Seifu; Lessanework

Attorney, Agent or Firm: Enable IP, P.C.

Background/Summary

TECHNICAL FIELD

(1) The present invention belongs to the technical field of preparation of semiconductor phosphides, specifically to a semiconductor phosphide injection synthesis system and a control method.

BACKGROUND ART

(2) Semiconductor phosphides mainly include indium phosphide, gallium phosphide, and other

semiconductor materials. An indium phosphide (InP) device has the characteristics of high frequency, high speed, irradiation resistance, low noise, and the like. Its operating frequency reaches 3 THz. When the operating frequency of the device is greater than 100 GHz, the InP demonstrates outstanding advantages. The InP has become a key semiconductor material of ultra-high-frequency and ultra-high-speed devices, and optoelectronic devices. With the development of terahertz, millimeter wave, optical communication, autonomous driving, Internet of things, and 5G/6G technologies in the future, the InP will play a greater role and achieve greater social benefits. A phosphide is extremely difficult to prepare since it has an extremely high saturated vapor pressure at its melting point.

(3) Synthesis methods for a phosphide mainly include horizontal diffusion synthesis and injection synthesis. Generally, the horizontal diffusion synthesis technology is simple, but has long synthesis cycle and low material purity, so it is hard to obtain a high-quality polycrystalline material. The phosphide injection synthesis technology is an excellent method for preparing polycrystals, which has the characteristics of high synthesis rate and high purity of a prepared material and has the disadvantage that in order to ensure the utilization rate of phosphorus, the injection synthesis rate is often required to be extremely low, so a phenomenon of explosion of a phosphorus source carrier is prone to occur. When the synthesis amount increases, the mass of red phosphorus in a phosphorus source carrier increases; it is difficult to achieve uniform heating of the red phosphorus. The thermal response capacity of a system is low, and the temperature control capacity of the system is low, so the risk of explosion of the phosphorus source carrier is increased. A polycrystalline material is the basis for preparing a single crystal material. Therefore, an injection synthesis device with high synthesis purity, high synthesis efficiency and high phosphorus utilization rate is urgently needed.

SUMMARY OF THE INVENTION

(4) The technical problem to be solved by the present invention is to provide a semiconductor phosphide injection synthesis system and a control method. By improving a device and method, the system stability can be improved, and an entire synthesis system achieves quantitative synthesis, which lowers the risk of explosion of a phosphorus source carrier.

(5) A technical solution adopted in the present invention: A semiconductor phosphide injection synthesis system includes a furnace body, a shielding carrier box arranged above the furnace body by virtue of a lifting mechanism, a phosphorus source carrier arranged in the shielding carrier box, an injection pipe arranged below the phosphorus source carrier, and a crucible arranged at an inner bottom of the furnace body in a matched manner. The phosphorus source carrier includes a phosphorus source carrier main body, a phosphorus source carrier upper cover, a heating element base arranged at an inner bottom of the phosphorus source carrier main body, and a heating element arranged on the heating element base; a heat insulation layer is wrapped on an outer wall of the phosphorus source carrier; and an induction coil is arranged between the heat insulation layer and an inner wall of the shielding carrier box.

(6) A control method implemented on the basis of the semiconductor phosphide injection synthesis system includes the following steps: step I, respectively loading red phosphorus and high-purity indium into the phosphorus source carrier and the crucible; then covering the high-purity indium with a boron oxide covering agent; vacuumizing the furnace body through a vent of the furnace body; and filling the furnace body with inert gas to complete the preparatory work; step II, heating the crucible by means of a main resistive heater to melt the high-purity indium into a melt; step III, heating a pressure measurement system by using an auxiliary heater; observing a solid boron oxide column through an observation window a, and recording a display temperature T1 of a thermocouple a and a scale value L1 on a scale after melting; calculating, according to a diameter of a pressure-equalizing pipe, an upper remaining space volume V1 of the pressure-equalizing pipe; and obtaining, according to a gas pressure formula, a value of pressure intensity P1 of gas in the pressure-equalizing pipe at the time; step IV, lowering the phosphorus source carrier towards the

melt by using the lifting mechanism until the injection pipe is close to a position from the bottom of the crucible and at the same time, a thermocouple b also enters an insertion slot; step V, electrifying the induction coil; observing bubbling of the injection pipe through the observation window b; recording a display temperature T2 of the thermocouple a and a scale value L2 on the scale when bubbling starts; calculating, according to the diameter of the pressure-equalizing pipe, an upper remaining space volume V2 of the pressure-equalizing pipe; and obtaining, according to a formula $P1V1/T1=P2V2/T2$, a value of pressure intensity P2 of the gas in the pressure-equalizing pipe at the time; step VI, keeping ΔP between 0.05 Pe and 0.1 Pe according to a pressure difference formula $\Delta P=P2-P0$, so as to control the bubbling rate of the injection pipe, where P0 represents a numerical value of a pressure gauge, and Pe represents a saturated vapor pressure at the melting point; a method for controlling the bubbling rate of the injection pipe including: adjusting, according to a display temperature feedback of the thermocouple b, a temperature in the phosphorus source carrier by adjusting the magnitude of a current of the induction coil in real time, thus ensuring that P2 in the phosphorus source carrier is constant, and accordingly achieving a constant bubbling rate of the injection pipe; and step VII, after the synthesis is completed, powering off the induction coil and the auxiliary heater, and resetting the phosphorus source carrier to force the injection pipe to be separated from the boron oxide covering agent.
(7) Beneficial effects achieved by the present invention are as follows: By use of the induction coil, a plurality of heating elements in the phosphorus source carrier generate heat to heat the red phosphorus, so that the red phosphorus is heated uniformly and is volatilized and injected into the melt; at the same time, a pressure and temperature measurement and balance system is arranged on the phosphorus source carrier and is used for measuring, in combination with the saturated vapor pressure of the phosphorus, a pressure and temperature inside the synthesis system with a corrosive atmosphere and an induction magnetic field, so that the entire synthesis system is monitorable and controllable. The device is particularly applicable to high-capacity synthesis; and the heating uniformity of the synthesis system can be improved, and the stability can be improved, so that the entire synthesis system achieves quantitative synthesis, and the risk of explosion of the phosphorus source carrier is lowered.

Description

BRIEF DESCRIPTION OF THE DRAWINGS
(1) FIG. **1** is a schematic structural diagram of the present invention;
(2) FIG. **2** is a schematic structural diagram of a phosphorus source carrier; and
(3) FIG. **3** is a schematic structural diagram of a pressure measurement system.
DETAILED DESCRIPTION OF THE INVENTION
(4) Referring to FIGS. **1-3**, semiconductor phosphide injection synthesis system includes a furnace body, a shielding carrier box **2** arranged above the furnace body by virtue of a lifting mechanism **20**, a phosphorus source carrier **11** arranged in the shielding carrier box **2**, an injection pipe **6** arranged below the phosphorus source carrier **11**, and a crucible **13** arranged at an inner bottom of the furnace body in a matched manner. The phosphorus source carrier **11** includes a phosphorus source carrier main body **11-2**, a phosphorus source carrier upper cover **11-1**, a heating element base **4** arranged at an inner bottom of the phosphorus source carrier main body **11-2**, and a heating element **12** arranged on the heating element base **4**; a heat insulation layer **7** is wrapped on an outer wall of the phosphorus source carrier **11**; and an induction coil **1** is arranged between the heat insulation layer **7** and an inner wall of the shielding carrier box **2**. A pressure gauge **23** is also arranged on an outer side of the furnace body.
(5) A pressure measurement system is arranged on the phosphorus source carrier upper cover **11-1**; the pressure measurement system includes a pressure-equalizing pipe **10-2** welded to the

phosphorus source carrier upper cover **11-1**, a solid boron oxide column **17** arranged in the pressure-equalizing pipe **10-2**, a pressure measurement sealing cap **10-1** with a thermocouple a**8**, and an auxiliary heater **21** arranged on an outer wall of the pressure-equalizing pipe **10-2**; the pressure measurement sealing cap **10-1** is welded to an upper end of the pressure-equalizing pipe **10-2**; a lower end of the pressure-equalizing pipe **10-2** is provided with an air inlet hole **10-4** communicated with the phosphorus source carrier **11**; an observation scale **10-3** is arranged on the pressure-equalizing pipe **10-2**; and an upper end surface of the furnace body is provided with an observation window a**18**.

(6) A thermocouple wire of the thermocouple a**8** is connected to a sensor on the outer side of the furnace body.

(7) A bottom of the phosphorus source carrier main body **11-2** is provided with an insertion slot **11-3** for accommodating a thermocouple b**22**; the thermocouple b**22** is "custom character"-shaped, an upper end of which is arranged in the insertion slot **11-3** and a left side of which is connected to the furnace body.

(8) An outer wall of the crucible **13** is provided with a main resistive heater **15** in a surrounding manner, and an observation window b**19** matched with the crucible **13** is arranged in the middle of the furnace body.

(9) A control method of the semiconductor phosphide injection synthesis system includes the following steps: step I, red phosphorus **3** and high-purity indium are respectively loaded into the phosphorus source carrier **11** and the crucible **13**; the high-purity indium is then covered with a boron oxide covering agent **14**; and the furnace body is vacuumized through a vent of the furnace body and is filled with inert gas to complete the preparatory work; step II, the crucible **13** is heated by means of the main resistive heater **15** to melt the high-purity indium into a melt; step III, the auxiliary heater **21** is used to heat the pressure measurement system **10**; a solid boron oxide column **17** is observed through the observation window a**18**, and a display temperature T1 of the thermocouple a**8** and a scale value L1 on the scale **10-3** after melting are recorded; an upper remaining space volume V1 of the pressure-equalizing pipe **10-2** is calculated according to a diameter of the pressure-equalizing pipe **10-2**; and a value of pressure intensity P1 of gas in the pressure-equalizing pipe **10-2** at this time is obtained according to a gas pressure formula; step IV, the phosphorus source carrier **11** is lowered towards the melt by using the lifting mechanism **20** until the injection pipe **6** is close to a position from the bottom of the crucible and at the same time, the thermocouple b**22** also enters the insertion slot **11-3**; step V, the induction coil **1** is electrified; bubbling of the injection pipe **6** is observed through the observation window b**19**; a display temperature T2 of the thermocouple a**8** and a scale value L2 on the scale **10-3** when bubbling starts are recorded; an upper remaining space volume V2 of the pressure-equalizing pipe **10-2** is calculated according to the diameter of the pressure-equalizing pipe **10-2**; and a value of pressure intensity P2 of the gas in the pressure-equalizing pipe **10-2** at this time is obtained according to a formula $P1V1/T1=P2V2/T2$; step VI, ΔP is kept between 0.05 Pe and 0.1 Pe according to a pressure difference formula $\Delta P=P=P2-P0$, so as to control the bubbling rate of the injection pipe **6**, where P0 represents a numerical value of the pressure gauge **23**, and Pe represents a saturated vapor pressure at the melting point; a method for controlling the bubbling rate of the injection pipe **6** including: adjusting, according to a display temperature feedback of the thermocouple b**22**, a temperature in the phosphorus source carrier **11** by adjusting the magnitude of a current of the induction coil **1** in real time, thus ensuring that P2 in the phosphorus source carrier **11** is constant, and accordingly realizing a constant bubbling rate of the injection pipe **6**; and step VII, after the synthesis is completed, the induction coil **1** and the auxiliary heater **21** are powered off, and the phosphorus source carrier **11** is reset to force the injection pipe **6** to be separated from the boron oxide covering agent **14**.

(10) During specific implementation, the thermocouple a**8** and the pressure measurement sealing cap **10-1** are welded together, and at the same time, two thermocouple wires are in no contact. The

pressure-equalizing pipe **10-2** and the phosphorus source carrier upper cover **11-1** are welded together. The solid boron oxide column **17** is put into the pressure-equalizing pipe **10-2**. The pressure measurement sealing cap **10-1** with the thermocouple a**8**, and the pressure-equalizing pipe **10-2** are welded together

(11) The heating element **12** is loaded on the heating element base **4** inside the phosphorus source carrier main body **11-2**. The red phosphorus **3** is then loaded into the phosphorus source carrier main body **11-2** according to desired synthesis mass, and the phosphorus source carrier upper cover **11-1** and the phosphorus source carrier main body **11-2** are welded together.

(12) The induction coil **1** is then put into the shielding carrier box **2**. Meanwhile, the heat insulation layer **7** is wrapped on an outer wall of the phosphorus source carrier **11**, and the phosphorus source carrier **11** wrapped with the heat insulation layer **7** is put into the induction coil **1**.

(13) The thermocouple wire of the thermocouple a**8** is connected to the sensor on the outer side of the furnace body. The observation window a**18** and the observation window b**19** are mounted on the furnace body.

(14) The high-purity indium and the boron oxide covering agent **14** are put into the crucible **13**, and the system is vacuumized to 10-5 Pa and is filled with the inert gas. The crucible **13** is heated through the main resistive heater **15**, so that the high-purity indium and the boron oxide covering agent **14** are melted, and the high-purity indium becomes a melt **16**.

(15) The auxiliary heater **21** is used to heat the pressure measurement system, which is observed through the observation window a**18** until the solid boron oxide column **17** is melted; after the thermocouple a**8** is stabilized, the temperature T1 and the scale value L1 on the scale **10-3** at this time are recorded. The volume V1 at this time is calculated according to the diameter of the pressure-equalizing pipe **10-2**. At this time, internal and external pressures are equalized, and the system pressure is P1.

(16) The phosphorus source carrier **11** is then lowered towards the melt **16** by using the lifting mechanism **20**, and the thermocouple b**23** is inserted into the insertion slot **11-3** until the injection pipe **6** is close to a position that is 3-5 mm above the bottom of the crucible.

(17) An alternating current is made to the induction coil **1**, and the bubbling of the injection pipe **6** is observed through the observation window b**19**. Moreover, the scale value L2 on the scale **10-3** is observed, and the temperature T2 at this time is recorded, thus obtaining the volume V2 at this time. The pressure P2 in the phosphorus source carrier at this moment is obtained. The P2 value is obtained according to the Clapeyron equation $P1V1/T1=P2V2/T2$. The bubbling rate is adjusted by a pressure difference $\Delta P=P2-P0$, and P0 is a numerical value on the pressure gauge **23**.

(18) The temperature of the phosphorus source carrier **11** is adjusted by the thermocouple b**22** to obtain the desired bubbling rate and a value of the pressure difference ΔP at this moment. The pressure inside the phosphor source carrier **11** is tested through the pressure measurement system **10**. Since a liquid boron oxide column **9** has poor thermal conductivity, the temperature feedback is insensitive. A temperature control system cannot feed back and control the power of the induction coil **1** through the thermocouple **8**. The power of the induction coil **1** is fed back through the thermocouple b**22**, and then the temperature in the phosphorus source carrier **11** is adjusted to adjust the numerical value of the pressure P2; the desired bubbling rate is obtained; and the optimal value of the pressure difference ΔP at this moment is obtained. As the number of phosphorus elements in the phosphorus source carrier **11** decreases, the pressure inside the phosphorus source carrier **11** will decrease. The power of the induction coil **1** is fed back and controlled by the temperature control system and the thermocouple b**22** to keep the pressure P2 in the phosphorus source carrier **11** constant.

(19) After the synthesis is completed, the current of the induction coil **1** and the auxiliary heater **21** drops to 0 A. The phosphorus source carrier **11** is lifted up by the lifting mechanism **20** to force the injection pipe **6** to be separated from the boron oxide covering agent **14**.

(20) After the furnace is dismantled, the system is vented to 1 atmosphere; the phosphorus source

carrier upper cover **11-1** is cut off; and phosphorus source carrier main body **11-2** is cleaned for next use. At the same time, the pressure measurement sealing cap **10-1** is cut off, and the thermocouple a**8** is maintained for the next use.

Claims

1. A semiconductor phosphide injection synthesis system comprising a furnace body, a shielding carrier box (**2**) arranged above the furnace body by virtue of a lifting mechanism (**20**), a phosphorus source carrier (**11**) arranged in the shielding carrier box (**2**), an injection pipe (**6**) arranged below the phosphorus source carrier (**11**), and a crucible (**13**) arranged at an inner bottom of the furnace body in a matched manner, wherein the phosphorus source carrier (**11**) comprises a phosphorus source carrier main body (**11-2**), a phosphorus source carrier upper cover (**11-1**), a heating element base (**4**) arranged at an inner bottom of the phosphorus source carrier main body (**11-2**), and a heating element (**12**) arranged on the heating element base (**4**); a heat insulation layer (**7**) is wrapped on an outer wall of the phosphorus source carrier (**11**); and an induction coil (**1**) is arranged between the heat insulation layer (**7**) and an inner wall of the shielding carrier box (**2**).
2. The semiconductor phosphide injection synthesis system according to claim 1, wherein a pressure measurement system is arranged on the phosphorus source carrier upper cover (**11-1**); the pressure measurement system comprises a pressure-equalizing pipe (**10-2**) welded to the phosphorus source carrier upper cover (**11-1**), a solid boron oxide column (**17**) arranged in the pressure-equalizing pipe (**10-2**), a pressure measurement sealing cap (**10-1**) with a thermocouple a (**8**), and an auxiliary heater (**21**) arranged on an outer wall of the pressure-equalizing pipe (**10-2**); the pressure measurement sealing cap (**10-1**) is welded to an upper end of the pressure-equalizing pipe (**10-2**); a lower end of the pressure-equalizing pipe (**10-2**) is provided with an air inlet hole (**10-4**) communicated with the phosphorus source carrier (**11**); an observation scale (**10-3**) is arranged on the pressure-equalizing pipe (**10-2**); and an upper end surface of the furnace body is provided with an observation window a (**18**).
3. The semiconductor phosphide injection synthesis system according to claim 2, wherein a thermocouple wire of the thermocouple a (**8**) is connected to a sensor on an outer side of the furnace body.
4. The semiconductor phosphide injection synthesis system according to claim 1, wherein a bottom of the phosphorus source carrier main body (**11-2**) is provided with an insertion slot (**11-3**) for accommodating a thermocouple b (**22**); the thermocouple b (**22**) is “custom character”-shaped, an upper end of which is arranged in the insertion slot (**11-3**) and a left side of which is connected to the furnace body.
5. The semiconductor phosphide injection synthesis system according to claim 1, wherein an outer wall of the crucible (**13**) is provided with a main resistive heater (**15**) in a surrounding manner, and an observation window b (**19**) matched with the crucible (**13**) is arranged in the middle of the furnace body.