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(54) Title: CHEMICAL VAPOR DEPOSITION (CVD) PROCESS FOR THERMALLY DEPOSITING SILICON CARBIDE FILMS ONTO A SUBSTRATE

(57) Abstract

A thermal CVD process for forming silicon carbide-type films onto a substrate comprising the steps of: (a) introducing di-tert-butylsilane vapor into a CVD reaction zone containing said substrate on which a silicon carbide film is to be formed; (b) maintaining the temperature of said zone and said substrate at about 400 °C to about 1,100 °C; (c) maintaining the pressure in said zone at about 0.1 to about 10 torr; and (d) passing said vapor into contact with said substrate for a period of time sufficient to form a silicon carbide-type film thereon.

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+ DESIGNATIONS OF "SU"

It is under examination in which parts of the former Soviet Union the designation of the Soviet Union has effect.

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CHEMICAL VAPOR DEPOSITION (CVD) PROCESS FOR THERMALLY DEPOSITING SILICON CARBIDE FILMS ONTO A SUBSTRATE

5 The present invention relates to a chemical vapor deposition (CVD) process for plasma depositing a silicon carbide film onto a substrate.

Chemical vapor deposition (CVD) is used through the microelectronics industry for semiconducting and 10 insulating thin film deposition. When films such as silicon carbide are deposited, silane (SiH_4) is generally used as the gaseous silicon source.

Silicon carbide (SiC) films are used in solar cells, as X-ray lithographic masks, and as hard coatings 15 on machining tools. Silicon carbide has the necessary electrical properties for use in solar cells and has good physical properties.

Silane is highly toxic and spontaneously ignites when exposed to air. It requires the use of expensive 20 gas cabinets and a cross-purging gas supply system. Special purging procedures are needed before introduction into deposition equipment. A number of silicon containing chemicals have been used or proposed as alternative silane sources. These include silicon 25 tetrachloride ($SiCl_4$), silicon tetrabromide ($SiBr_4$), silicon tetrafluoride (SiF_4), dichlorosilane (SiH_2Cl_2), and disilane (Si_2H_6). All halogen-containing silanes are toxic and corrosive themselves in addition to producing toxic and corrosive 30 by-products. Disilane is a flammable, toxic gas that requires similar handling procedures to silane. Also, use of these alternative silicon sources requires an additional reactant such as methane to supply carbon to the deposition process to form the silicon carbide

film. Other chemicals such as tetraethylorthosilicate [TEOS, $Si(OC_2H_5)_4$] and tetramethylcyclotetra-siloxane (TMCTS, $C_4H_{16}Si_4O_2$) can only be used for oxide deposition.

5 Accordingly, there is a need for better alternatives to silane as a precursor for depositing silcon carbide films in CVD processes.

U.S. Patent No. 4,459,338, which issued to Angelini, et al. on July 10, 1984, teaches a CVD process

10 for applying silicon carbide onto a film by contacting the substrate with a gaseous mixture of methylsilane and an inert gas while heating the gaseous mixture and the substrate to about 800°-1,050°C.

U.S. Patent No. 4,810,526, which issued to Ito, et

15 al., on March 7, 1989, teaches a CVD process for applying silicon carbide onto a substrate in a heated furnace by introducing a feedstock gas containing a single silicon and carbon source (e.g., trichloromethylsilane) into the heated furnace under a

20 vacuum.

U.S. Patent No. 4,923,716, which issued to Brown, et al., on May 8, 1990, teaches a CVD process for depositing silicon carbide from a vapor source having a single molecular species that has both silicon and

25 carbon atoms in equal numbers. Preferred molecular sources include $H_3SiCH_2CH_2SiH_3$; a silacycloalkane of the form $(-SiH_2CH_2-)_p$, where p is 2, 3, 4, or 5, or a cyclic structure of the form $[-SiH(CH_3)-]_q$, where q is 4 or 5.

30 Separately, di-tert-butylsilane (DTBS) is a known chemical with a Chemical Abstracts registry number [30736-07-3]. Processes for making DTBS are disclosed by Wataname, et al. "A Simple and Convenient Method for Preparing Di-t-Butyl Silanes", Chemistry Letters, pp.

35 1321-1322, 1981; Doyle, et al. "Hindered Organosilicon Compounds, Synthesis and Properties of Di-tert-butyl-,

Di-tert-butylmethyl-, and Tri-tert-butylsilanes", J. Am. Chem. Soc. 97, pp. 3777-3782 (1975); and Triplett, et al. "Synthesis and Reactivity of Some t-Butyl-Disilanes and Digermanes", Journal of Organometallic Chemistry,
5 Vol. 107, pp. 23-32 (1976). DTBS has been used as a silylation agent to hydroxy compounds (CA 101:91218v) and as an intermediate in the production of di-tert-butyldichlorosilane (CA 98:126375t).

Also, DTBS has been used as a silicon source for
10 depositing silicon nitride or silicon dioxide by either thermal or plasma CVD processes. See U.S. Patent Nos. 4,877,641 and 4,877,651, both of which issued to Thomas S. Dory on October 31, 1989.

Di-tert-butylsilane (DTBS) is an air-stable,
15 noncorrosive liquid. It is soluble in many organic solvents and does not react with water. Its high vapor pressure at room temperature allows for easy introduction into CVD reactors. No gas cabinets or cross-purging systems are needed in order to use this
20 chemical in CVD reactors. The decomposition by-products are not corrosive in nature. Also, in the deposition of silicon carbide, DTBS can be used by itself to form the film since it contains the required carbon to form silicon carbide. Di-tert-butylsilane represents an
25 air-stable liquid source that can be used for the deposition of silicon. This eliminates the need for using the flammable, toxic chemical, silane, and eliminates the need for an additional reactant to supply carbon for for the deposition process.

30 Accordingly, the present invention is directed to a thermal CVD process for forming silicon carbide-type films onto a substrate comprising the steps of:

(a) introducing di-tert-butylsilane gas into a CVD reaction zone containing said substrate on which a
35 silicon carbide film is to be formed;

(b) maintaining the temperature of said zone and said substrate from about 100°C to about 400°C.;

(c) maintaining the pressure in said zone from about 0.1 to about 10 torr; and

5 (d) passing said gas into contact with said substrate for a period of time sufficient to form a silicon carbide-type film thereon.

The CVD process of this invention may be used to produce silicon carbide-type or SiC type films having an 10 optimum refractive index in the range from about 2.6 ± 0.4. The lower the refractive index in this range, the higher the carbon percentage; and the higher the refractive index in this range, the higher the Si percentage. The terms "silicon carbide-type films" and 15 "SiC-type films", as used herein, mean films formed with a refractive index in the above optimum range.

Substrates may be any material on which a silicon carbide-type film is desired, e.g., silicon wafers, plastic, resin, glass, or metal objects or films; GaAs 20 layers; or any semiconductor layer or device, preferably those employing Groups II to V of the Periodic Table of Elements or compounds thereof. The substrate is heated to the reaction temperature by a resistance element in a reaction chamber into which the vapor is introduced. In 25 a preferred embodiment of the process, the reaction chamber is prepared for film production by the preliminary step of passivating the chamber with a silicon carbide-type coating of this invention.

While not critical, it is preferred to maintain 30 the reaction chamber isothermal, by which is meant having temperature variations throughout of less than 2°C, preferable ±1°C. The reactant vapor is input at a sufficient distance from the wafers to be coated to permit the vapor to reach reaction temperature. 35 Compared to the wafer mass, the vapor, at its input temperature, will not appreciably cool the wafer.

The vapor is introduced in a substantially laminar flow over the substrate surface. The residence time over the substrate is kept short to eliminate substantial concentration variations over the wafer. 5 The substrate, typically an Si wafer, is preferably confined in a manner so as to provide a reaction chamber wall to wafer edge spacing and wafer to adjacent wafer spacing, such that the silicon carbide-type film produced by the process of this invention is 10 substantially uniform across the wafer surface, i.e., does not exhibit substantial concavity (edge build-up) or convexity (center mounding). An example of appropriate spacing of wafer to wafer and wafer to chamber wall are discussed in Becker, et al. 15 "Low-Pressure Deposition of High-Quality SiO_2 films by Pyrolysis of Tetraethylorthosilicate". J. Vac Soc. Techno. B, Vol. 6, No 6 pp 1555-1563 (Nov./Dec., 1987). Film uniformity obtained preferably exhibits less than ± 3% thickness variation, both within (across) the wafers, 20 and from wafer to wafer in a batch or production run.

Typical gas flow rates may be on the order of from 10 to about 400 standard cc/min. for the DTBS. The preferred gas flow rate range is about 20 to about 200 sccm.

25 As mentioned above, the reaction chamber pressures are controlled in the range of from about 0.1 torr to about 10 torr. The preferred range being from about 0.5 to 5 torr. As also mentioned above, the reaction temperature is from about 400°C to 1,100°C. The 30 preferred temperature range is about 500°C to about 750°C.

The film formation rate is typically in the range of from about 10 to about 500 Angstroms/minute with typical operating rates of from about 15-300 Å/min., 35 with the optimum being about 20-200 Å/min. at an optimum pressure of about 0.75-2.0 torr at an optimum temperature range from about 550°C to 650°C.

The following example further illustrates the present invention. All parts and percentages are by weight unless explicitly stated otherwise.

EXAMPLE 1

5 THERMAL DEPOSITION OF SILICON CARBIDE (SiC) EMPLOYING DTBS AS A REACTANT

For this example, a three zone horizontal tube furnace with a four inch silicon wafer capacity manufactured by CVD Equipment Corporation of Deer Park,
10 NY equipped with a quartz furnace tube and quartz wafer boat was used. The quartz tube was connected to a Model 88102119HQ vacuum pumping system manufactured by Alcatel Vacuum Products of Hingham, MA. Gas control to the system was accomplished by use of a DynaMass flow
15 control system (Model DM-1400) and UltraFlo mass flow controllers (Model UC2-31) manufactured by Vacuum General of San Diego, CA. Vapor control to the system was accomplished by use of a Model LC2-41VS01 mass flow controller also manufactured by Vacuum General of San
20 Diego. Pressure control of system was accomplished by use of an AdapTorr throttle valve control system (Model AC-2) and a motorized throttle valve attached to the exit end of the furnace tube (Model MDVX-015) also manufactured by Vacuum General of San Diego. Liquid
25 di-tert-butylsilane was contained in a 1.2 liter capacity stainless steel ampule, and the temperature of the ampule was maintained at 40°C by using a source controller (Model 875) manufactured by Olin Hunt Corporation of Seward, IL. Vapor from the DTBS was fed
30 to the vapor mass flow controller. The quartz wafer boat was fitted inside the quartz tube and held four inch silicon wafers in a vertical orientation. The loaded quartz wafer boat was placed in the second zone of the furnace.

After loading the furnace (previously heated to 550°C in three zones) with the quartz boat and 7 wafers, the vacuum pumping system was used to evacuate the furnace tube to a base pressure of 0.030 torr. DTBS
5 vapor at a flow rate of 100 sccm was introduced into the furnace tube through an inlet attached to the door at the first zone of the furnace. Soon after the DTBS flow was started, the pressure in the furnace tube was brought up to 1.0 torr by means of the throttle valve.

10 Reaction and decomposition of the DTBS vapor formed silicon carbide surfaces on the silicon wafers in the quartz boat. After 30 minutes, the throttle valve was fully opened, the DTBS flow was stopped, and nitrogen gas introduced to purge the system. After
15 flushing the system for a sufficient time, the system was vented and the quartz boat removed.

The silicon carbide films on the silicon wafers were examined. A sputtered AUGER profile was done on a sample of the film. The results of the profile
20 indicated that the average silicon carbide thickness was 585 Å. The average atomic concentration of silicon and carbon in the film was measured at 47% each with the remainder being oxygen. These results indicate that a good silicon carbide film was deposited on the silicon
25 wafers.

What Is Claimed Is:

1. A thermal CVD process for forming silicon carbide-type films onto a substrate characterized by the steps of:

(a) introducing di-tert-butylsilane vapor into a
5 CVD reaction zone containing said substrate on which a silicon carbide film is to be formed;

(b) maintaining the temperature of said zone and said substrate at about 400°C to about 1,100°C;

(c) maintaining the pressure in said zone at about
10 0.1 to about 10 torr; and

(d) passing said vapor into contact with said substrate for a period of time sufficient to form a silicon carbide-type film thereon.

2. The thermal CVD process of Claim 1, wherein the flow rate of said di-tert-butylsilane into said zone is from about 25 sccm to about 400 sccm.

3. The thermal CVD process of Claim 1, characterized in that said zone temperature and said substrate temperature are from about 500°C to about 750°C.

4. The thermal CVD process of Claim 1, characterized in that said zone pressure is from about 0.5 torr to about 5 torr.

5. The thermal CVD process of Claim 1, characterized in that said di-tert-butylsilane film rate is formed at a rate from about 10 to about 500 Angstroms/minute.

6. The thermal CVD process of Claim 1, characterized in that said substrate is selected from

the group consisting of resin objects or films, glass objects or films, metal objects or films, GaAs layers,
5 and semiconductor layers or devices.

7. A thermal CVD process for forming silicon carbide-type film onto a substrate characterized by the steps of:

(a) introducing di-tert-butylsilane vapor into a
5 CVD reaction zone containing said substrate on which a silicon carbide film is to be formed; the flow rate of said di-tert-butylsilane into said zone is from about 10 sccm to about 400 sccm;

(b) maintaining the temperature of said zone and
10 said substrate at about 500°C to about 750°C;

(c) maintaining the pressure of said zone at about 0.5 torr to about 5 torr; and

(d) passing said gas into contact with said substrate for a period of time sufficient to form a
15 silicon carbide-type film thereon, the rate of film formation being at about 10 to about 500 Angstroms per minute.

8. The thermal CVD process of Claim 7, characterized in that said flow rate of di-tert-butylsilane is from about 20 to about 200 sccm.

9. The thermal CVD process of Claim 7, characterized in that said temperature is from about 550°C to about 650°C.

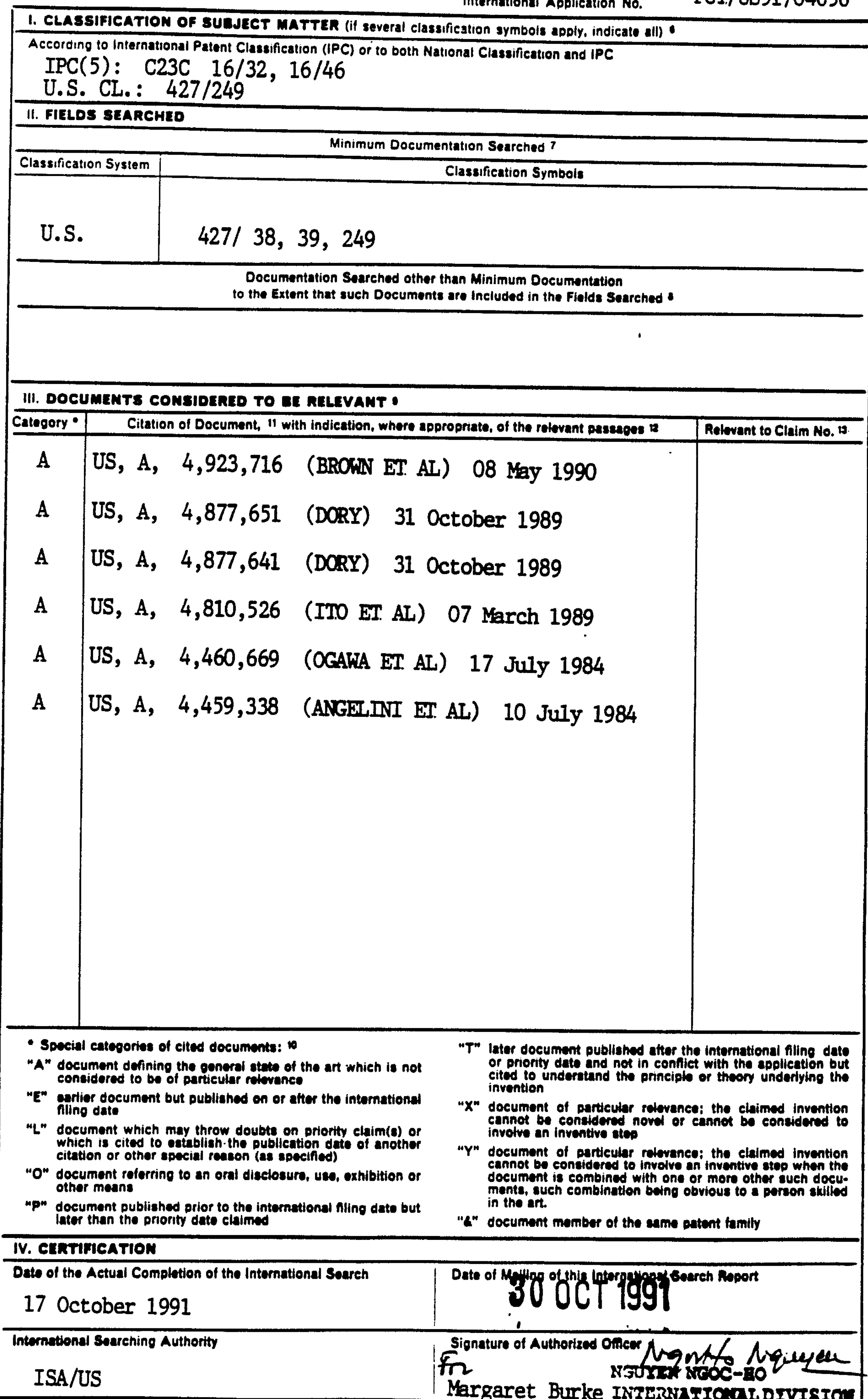
10. The thermal CVD process of Claim 7, characterized in that said pressure is from about 0.75 to about 2.0 torr.

11. The thermal CVD process of Claim 7, characterized in that said film formation rate is from about 15 to about 300 Angstroms per minute.

12. The thermal CVD process of Claim 7, characterized in that said substrate is selected from the group consisting of resin objects or films, glass objects of films, metal objects or films, GaAs layers,
5 and semiconductor layers or devices.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/04656



I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C23C 16/32, 16/46
U.S. CL.: 427/249

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	427/ 38, 39, 249

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4,923,716 (BROWN ET AL) 08 May 1990	
A	US, A, 4,877,651 (DORY) 31 October 1989	
A	US, A, 4,877,641 (DORY) 31 October 1989	
A	US, A, 4,810,526 (ITO ET AL) 07 March 1989	
A	US, A, 4,460,669 (OGAWA ET AL) 17 July 1984	
A	US, A, 4,459,338 (ANGELINI ET AL) 10 July 1984	

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17 October 1991	30 OCT 1991

International Searching Authority	Signature of Authorized Officer
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