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<p>(21) International Application Number: PCT/SE93/00072</p> <p>(22) International Filing Date: 1 February 1993 (01.02.93)</p> <p>(30) Priority data: 9200555-2 25 February 1992 (25.02.92) SE</p> <p>(71) Applicant (for all designated States except US): MARK-POINT DEVELOPMENT AB [SE/SE]; Södra Säterigatan 20, S-417 11 Göteborg (SE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : VONASEK, Jiri [SE/SE]; Gullbringa Pl.2922, S-442 95 Kungälv (SE). LARSSON, Stig-Göran [SE/SE]; Klintmossevägen 14, S-430 50 Källered (SE). ANDERSSON, Ove [SE/SE]; Hammarvägen 162, S-421 65 Västra Förlunda (SE).</p>		<p>(74) Agents: GRAUDUMS, Valdis et al.; Albihn West AB, Box 142, S-401 22 Göteborg (SE).</p> <p>(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: A METHOD OF COATING A PIEZOELECTRIC SUBSTRATE WITH A SEMI-CONDUCTING MATERIAL AND A METHOD OF PRODUCING A DROPLET EJECTOR ARRANGEMENT INCLUDING THE COATING METHOD</p> <div style="text-align: center;"> </div> <p>(57) Abstract</p> <p>A method of coating a piezoelectric substrate with a semi-conducting material by chemical vapour deposition so as to form a coated object which can be easily bonded to another material such as glass. Chemical vapour deposition of a semi-conducting material is performed such that a layer of desired smoothness is deposited on the piezoelectric substrate. Such a method is particularly applicable for piezoceramic ink-jet printers.</p>		

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5 **TITLE:**

A method of coating a piezoelectric substrate with a semi-conducting material and a method of producing a droplet ejector arrangement including the coating method

TECHNICAL FIELD:

10 The present invention relates to a method of coating a piezoelectric substrate, preferable a piezoceramic wafer, with a substantially uniform layer of a semi-conducting material. The invention further relates to a method of producing a droplet ejector arrangement according to the
15 preamble of claim 13.

BACKGROUND OF THE INVENTION:

In his work in the field of piezoelectric pumps, the present applicant has recognised a need for a means of
20 coating piezoelectric substrates with a semi-conducting material which is susceptible to doping or other techniques to impart electrically-conducting properties to the coating. Such substrates are particularly suitable for use in ink-jet printing devices of the type described in
25 Applicant's International patent application No. PCT/EP90/02119, filed 6 December, 1990, in which a piezoceramic wafer having planar opposite first and second surfaces has grooves or channels extending inwardly therein. The groove or grooves of the first face lie offset
30 to the groove or grooves of the second face with the grooves partially overlapping in the direction of their depth. Each groove of one of the faces is intended to function as a droplet ejector channel. This is achieved by providing defined areas of the piezoceramic wafer with a
35 conducting coating, thereby forming electrodes for each ejector channel. Thereafter the material is polarized by applying an electrical voltage between the electrodes. An

electrical pulse is subsequently applied across the electrodes, causing a rapid decrease in volume of the ejector channel and thereby effecting discharge of the liquid from within the channel. Discharge of the liquid in a longitudinal direction is assured by covering the open longitudinal extension of the ejector channels with a cover plate. This cover plate also serves to impart stability to the piezoceramic wafer.

Whilst the above-described type of ink-jet printing device offers, in theory, a much more versatile printing system, its usefulness has until now been hampered by the difficulty in obtaining a satisfactory bond between the cover plate and the coated piezoceramic wafer. Satisfactory bonding is very much dependent on the smoothness of the surfaces which are to be bonded. It is relatively easy to obtain an adequately smooth surface on the cover plate since in most cases the cover plate is made from glass. Difficulties arise, however, with the coated piezoceramic wafer. A satisfactory degree of smoothness can be imparted on the piezoceramic wafer itself, and this must then be maintained after the application of the electrode coating. Thus, the coating process must result in a piezoceramic wafer having a sufficiently smooth surface electrode coating.

When electrode application methods performed by the present applicant have resulted in a crystalline coating of semi-conducting material, it has been found to be too uneven to be bonded by, for example, anodic bonding unless subjected to subsequent smoothing operations. Attempts have been made to bond for example a crystalline silicium-coated piezoceramic wafer obtained by chemical vapour deposition(CVD) to glass by distributing adhesive over the glass cover plate by centrifugal spinning. In order to avoid the need for an adhesive agent, trials have been

conducted on piezoceramic wafers coated by sputtering. Whilst sputtering results in a relatively smooth coating, sputtering techniques cannot provide an ejector channel for an ink-jet printing device whose side walls are adequately coated with electrode material.

SUMMARY OF THE INVENTION:

It is therefore an object of the present invention to provide a method of coating a piezoelectric, preferably piezoceramic, substrate, preferably in wafer form, with a substantially uniform layer of a semi-conducting material and which resulting layer is sufficiently smooth to allow bonding between the thus coated piezoelectric substrate and a cover plate.

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This object is achieved according to the present invention by a method according to claim 1.

It is a further object of the present invention to provide a method of producing a droplet ejector arrangement having at least one ejector channel in a wafer of piezoceramic material.

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This object is achieved according to claim 11.

25

Further advantageous adaptations of these methods are detailed in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1 is a schematic cross-sectional view through a droplet ejector arrangement whose piezoceramic wafer is coated with a semi-conducting material in a method according to the present invention, and

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Fig. 2 is a block diagram representing apparatus suitable for carrying out the method according to the present invention.

5 BEST MODE OF CARRYING OUT THE INVENTION:

The droplet ejector arrangement according to Fig. 1 comprises a piezoelectric, preferably piezoceramic, wafer 1 having formed therein on one side a longitudinally extending ejector channel 2 and, on the opposite side, a pair of longitudinally extending separation grooves 3. As is clear from Fig. 1, the separation grooves lie offset relative to the ejector channel and partially overlap the channel in the direction of their depth. In a manner known from PCT/EP90/02119, the ejector channel 2 is provided with an ejector nozzle 4. The ejector channel 2 is delimited along its longitudinally extending opening by a cover plate 5, in the shown example made from glass.

As indicated by the heavier lines, the piezoceramic wafer is provided with a layer 6 of a semi-conducting material on the majority of its surfaces. More specifically, the layer of semi-conducting material coats two distinct regions A, B of the wafer 1. The region A includes the adjacent side wall surfaces 7 of the separation grooves 3 and the outwardly facing surface 8 of the wafer between said wall surfaces 7. Accordingly, a U-shaped region is coated, which region A acts as a first electrode for the ejector arrangement. The region B includes all the remaining peripheral surfaces exposed in cross-section, with the exception of the base surface 9 of each separation groove 3. This region B forms a second electrode for the ejector arrangement, which electrode coats all the surfaces of the ejector channel 2.

35 Chemical vapour deposition apparatus suitable for performing the method of obtaining a semi-conducting

material coating on a piezoelectric substrate in accordance with the present invention is shown in schematic form in Fig. 2. The apparatus is in the form of a system 10 comprising a heated chamber 11 in which deposition of a semi-conducting material on one or more piezoelectric substrates 12 takes place. The chamber 11 is provided with not shown heating means to allow a temperature of up to 750°C to be attained. Two supply conduits 13, 14 are shown entering the chamber 11. One conduit 13 is connected to a supply 15 of a semi-conducting material-bearing gas such as silane via a pressure valve 16. In one embodiment according to the present invention the other conduit 14 is connected to a supply 17 of a doping agent such as phosphine, again via a pressure valve 18. A conduit 19 is shown exiting the chamber 11 and is connected to a vacuum generator 20 in the form of a pump or the like. An exhaust conduit 21 runs from the vacuum generator 20 to a burner assembly 22 in which exhausted gases are burnt off.

In accordance with the method of the present invention, one or more piezoelectric, preferably piezoceramic, substrates, preferably in wafer form, are placed within the chamber 11. The temperature within the chamber is raised and the pressure therein is reduced. When the temperature and pressure have reached predetermined suitable levels, the gas, e.g. silane, is admitted to the chamber. As a result of the heat and pressure conditions, a layer of semi-conducting material, in this case silicium, is deposited on the piezoceramic substrates. The surface smoothness of the deposited material has been found to be dependent primarily on the temperature in the chamber, with smoother surfaces being obtainable at lower temperatures. Indeed, under certain conditions, the resulting deposited layer can be said to be amorphous in its structure. The rate of deposition is dependent on the temperature and pressure parameters as well as the flow rate of semi-conducting

material-carrying gas into the chamber, though typically can lie between 500 and 5 000 angstrom/hour. The resulting hydrogen is removed from the chamber and is burnt off.

5 Semi-conducting material-coated piezoceramic wafers produced in accordance with the above method are eminently suitable for direct bonding to a cover plate when the semi-conducting material coating is amorphous, and thereby much smoother than crystalline coatings. Furthermore, the above-
10 described chemical vapour deposition method results in a very uniform semi-conducting material coating over all the exposed surfaces of the substrate, substantially independent of the orientation of the substrate in the chamber.

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Tests have shown that the pressure within the chamber may be maintained between 100 and 1 500 mTorr. Very favourable results have been achieved with a pressure of 250 mTorr. A preferred temperature range is 300 to 700°C, with
20 particularly favourable results being obtained between 500 and 530°C, especially at 520°C.

For many applications it is advantageous if the semi-conducting material coating can be doped at the same time
25 that it is deposited on the substrate. If this is desired, then the semi-conducting material must be susceptible to doping. Suitable materials are i.a. silicium and germanium. In order to achieve doping, in accordance with a preferred adaptation of the present invention, a doping agent in
30 gaseous form is admitted to the chamber 11 via the conduit 14 simultaneously with the silane. A suitable doping agent-carrying gas may be phosphine or boron. In Fig. 2 the doping agent-carrying gas is shown as being supplied to the chamber 11 via the conduit 1, though it is of course
35 conceivable that the two gases be mixed before entering the chamber. A suitable quantity of doping agent-carrying gas

is 0.01 to 1.0% by volume of the semi-conducting material-carrying gas. Whilst it is preferable to dope the semi-conducting material during deposition, it is also feasible to dope the semi-conducting material coating in a separate subsequent step.

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To ensure an improved adhesion of the semi-conducting material coating to the substrate, it is often advantageous to supply hydrogen to the chamber, preheated to around 500°C, with the substrate in situ before the coating material-carrying gas is admitted so as to aggressively clean the surfaces of the substrate.

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Alternatively, or in combination with the above, the surfaces of the substrate can be effectively deactivated by raising the temperature in the chamber 11 to around 750°C for a short period before deposition commences. The temperature is then reduced to the desired level, dependent on the degree of surface smoothness and deposition rate which is required, and the silane or other suitable gas, with or without a doping agent, introduced.

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Once a sufficiently thick layer of the semi-conducting material has been deposited on the substrate or substrates, the chamber 11 and the outlet/exhaust conduits 19, 21 may be flushed with nitrogen.

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In accordance with the present invention, a droplet-ejector arrangement of the type shown in Fig. 1 can be produced in the following manner. Firstly, longitudinally extending grooves 2, 3 are formed on either side of a non-polarized piezoceramic wafer 1. The grooves may be formed using a circular saw or some other form of cutting implement, or may be formed by moulding or pressing. In the shown example only one ejector channel 2 is formed, but it will be clear

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to the skilled man that a plurality of such ejector channels can be provided if so desired.

5 Once the ejector channel and separation grooves have been formed, the wafer is placed in the heating chamber as shown in Fig. 2 and coating takes place in accordance with that described above. Once an adequately thick layer of doped semi-conducting material is deposited on the wafer, the wafer is withdrawn from the chamber 11 and the deposited material is removed from the base surface 9 of each separation groove 3. Thereafter the wafer is polarized by applying a voltage between the electrodes of the ejector channel 2. The coated wafer is then bonded directly to the cover plate 5, for example made from glass, without any further treatment. A preferred bonding method is anodic bonding in which a voltage is applied across the cover plate 5 and the electrode covering the region B of the wafer to create a positive electric field from the coating material to the cover plate.

20 In a further embodiment according to the present invention, in order to impart electrically-conducting properties to the semi-conducting material coating, instead of admitting a doping agent-carrying gas to the chamber 11, a vaporized metal is admitted once the semi-conducting material has been deposited on the wafer. Suitable metals are palladium, nickel and tungsten. The precipitated metal is then bonded to the semi-conducting material layer by sintering.

30 Naturally, the present invention is not restricted to that described above, but may be varied within the scope of the following claims. For example, although the described coating methods are eminently applicable to the manufacturing of ink-jet printer heads, it is to be understood that the claimed method may be applied to any use of electroded piezoelectric material.

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CLAIMS:

10 1. A method of coating a piezoelectric, preferably piezoceramic, substrate (12), preferably in wafer form, with a substantially uniform layer (6) of a semi-conducting material such as silicium or germanium, wherein said substrate (12) is placed in a heated deposition chamber (11) at reduced pressure and a semi-conducting material-bearing gas is admitted to said chamber at pressure and temperature conditions such that a layer of semi-conducting material of desired smoothness is deposited on said substrate by chemical vapour deposition.

20 2. A method according to claim 1, characterized in that the pressure in the chamber (11) during deposition is maintained between 100 and 1 500 mTorr, preferably 250 mTorr.

25 3. A method according to claim 1 or 2, characterized in that the temperature in the chamber (11) during deposition is between 300 and 700°C, preferably between 500 and 530°C, and most preferably 520°C.

30 4. A method according to any of the preceding claims, characterized in that a doping agent in gaseous form is admitted to the chamber (11) simultaneously with the semi-conducting material-bearing gas.

5. A method according to claim 4, characterized in that said doping agent is mixed with the semi-conducting material-bearing gas in a quantity 0.01 to 1.0% by volume of the semi-conducting material-carrying gas

6. A method according to any of claims 1 to 3, characterized in that the semi-conducting material coating is doped after deposition.

7. A method according to claim 5 or 6, characterized in that said doping agent is phosphine or boron.

8. A method according to any of claims 1 to 3, characterized in that a vaporized metal, such as palladium, nickel or tungsten, is admitted to the chamber (11) once the semi-conducting material has been deposited on the substrate (12).

9. A method according to claim 7, characterized in that metal precipitated on the semi-conducting material layer is bonded thereto by sintering.

10. A method according to any of the preceding claims, characterized in that the substrate (12) is exposed to a temperature of between 650 and 750°C before deposition commences.

11. A method according to any of claims 1 to 10, characterized in that the chamber (11) is purged with hydrogen at approximately 500°C to clean the substrates before deposition commences.

12. A method according to any of the preceding claims, characterized in that the chamber (11) and other ancillary components (19,20,21,22) are flushed with nitrogen after the coated substrate has been removed from the chamber.

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13. A method of producing a droplet ejector arrangement comprising:

- 10 i) forming at least one longitudinally extending groove which is intended to serve as an ejector channel (2) for a liquid in a first planar face of a piezoelectric, preferably piezoceramic, wafer (1), regions of which wafer serve as a transducer for the ejector channel, and forming grooves (3) in a second planar face of said wafer opposite said first face such that said latter grooves lie offset relative to the ejector channel or channels (2) in said first face and partially overlap therewith in the direction of their depth, said ejector channel or channels (2) being provided with a nozzle or nozzles (4) at one end thereof;
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- ii) coating the exposed surface of the wafer (1) with a semi-conducting material to form electrodes;
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- iii) removing the semi conducting material from undesired regions (10);
- iv) polarizing each transducer by applying a voltage between its electrodes (A,B),

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characterized in that said coating is achieved by the method according to any one of claims 1 to 12.

5 14. A method according to claim 13, characterized in that a cover plate (5) is bonded to said coated wafer so as to delimit the longitudinal opening of said ejector channel or channels (2).

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15. A method according to claim 14, characterized in that said bonding is achieved by anodic bonding.

15 16. A method according to claim 14 or 15, characterized in that said cover plate (5) is made from glass.

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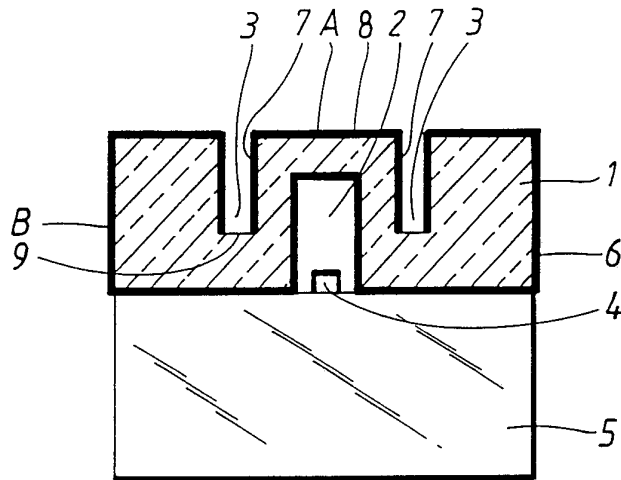


FIG. 1

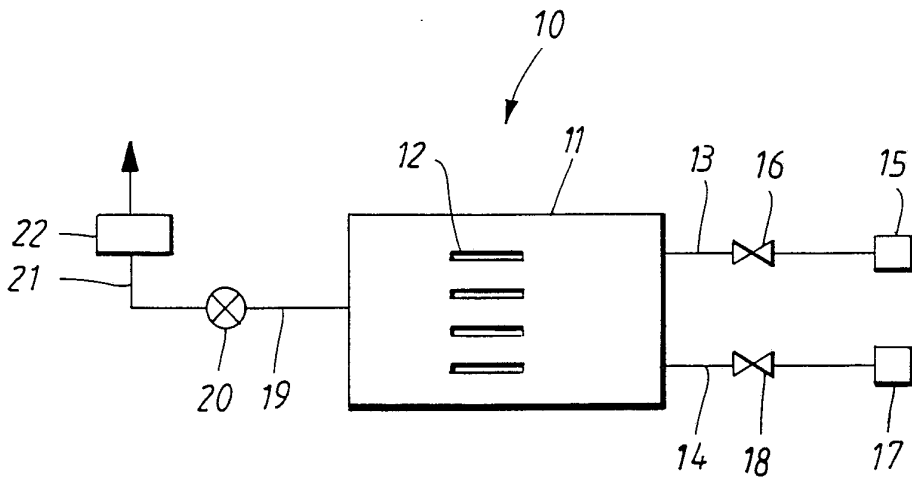


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 93/00072

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C23C 16/24, B41J 2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B41J, C23C, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0143701 (THOMSON-CSF), 5 June 1985 (05.06.85) --	1,3,4
X	EP, A2, 0431338 (MATSUSHITA ELECTRIC INDUSTRIAL CO, LTD.), 12 June 1991 (12.06.91), column 10, line 51 - column 12, line 36 --	1
P,X	WO, A1, 9210367 (MARKPOINT DEVELOPMENT AB), 25 June 1992 (25.06.92), page 12, line 3 - line 11, claim 21 --	1,13
A	EP, A2, 0296702 (DOW CORNING CORPORATION), 28 December 1988 (28.12.88) --	1

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search

17 May 1993

Date of mailing of the international search report

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4819014 (TAKESHI YASUHARA ET AL), 4 April 1989 (04.04.89), column 4, line 23 - line 32, figure 2 ----- -----	1

INTERNATIONAL SEARCH REPORT
Information on patent family members

31/03/93

International application No.
PCT/SE 93/00072

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0143701	05/06/85	FR-A,B- 2555206	24/05/85
EP-A2- 0431338	12/06/91	JP-A- 3153359	01/07/91
WO-A1- 9210367	25/06/92	NONE	
EP-A2- 0296702	28/12/88	AU-B- 610153 AU-A- 1476488 JP-A- 1009614 US-A- 4762808	16/05/91 22/12/88 12/01/89 09/08/88
US-A- 4819014	04/04/89	DE-A,C- 3630206 DE-C- 3645017 JP-A- 62198464 US-A- 4752788 JP-A- 62198465 JP-A- 62198466 JP-A- 62238756 JP-A- 63045056 JP-A- 63045057 JP-A- 62056150	19/03/87 12/07/90 02/09/87 21/06/88 02/09/87 02/09/87 19/10/87 26/02/88 26/02/88 11/03/87