

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 January 2002 (10.01.2002)

PCT

(10) International Publication Number
WO 02/03438 A1

(51) International Patent Classification⁷: **H01L 21/28**

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(21) International Application Number: PCT/IB01/01229

(22) International Filing Date: 6 July 2001 (06.07.2001)

(81) Designated States (*national*): JP, KR, SG.

(25) Filing Language: English

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(26) Publication Language: English

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

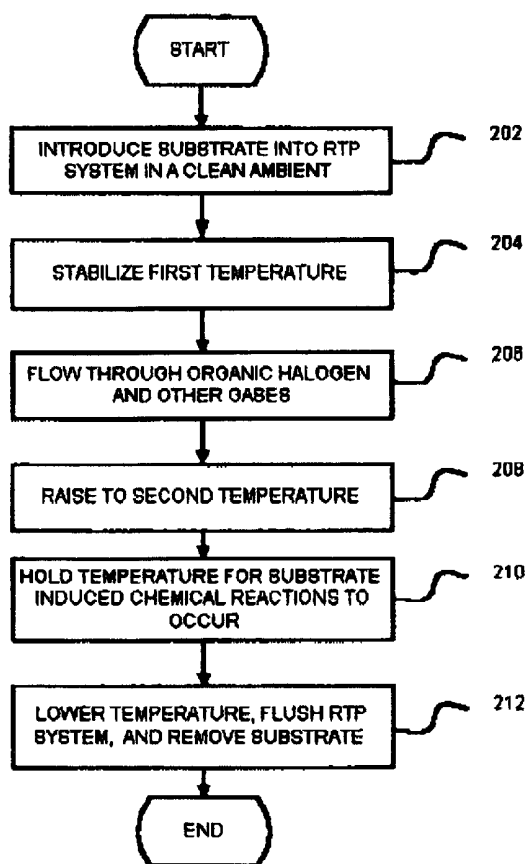
(30) Priority Data:

60/216,417 6 July 2000 (06.07.2000) US
09/654,789 15 September 2000 (15.09.2000) US

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** METHOD AND APPARATUS FOR RAPID THERMAL PROCESSING (RTP) OF SEMICONDUCTOR WAFERS



(57) **Abstract:** A system, method, and apparatus is presented for processing a semiconductor substrate in an RTP system, where the surface of the substrate is contacted with an organic halogen containing gas. The substrate temperature is greater than the temperature at which the organic halogen gas dissociates to give free halogen. In the most preferred embodiment, oxygen is also present and a film of chlorinated silicon dioxide is grown on a silicon substrate.

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Method and apparatus for rapid thermal processing (RTP) of semiconductor wafers

FIELD OF THE INVENTION

The field of the invention is semiconductor processing. In particular, method and apparatus for creating extremely high quality chlorinated films on semiconductor wafer surfaces in a Rapid Thermal Processing (RTP) environment are disclosed.

BACKGROUND OF THE INVENTION

The incorporation of a few atomic percent of chlorine in films used in modern semiconductor wafer processing has been shown to have beneficial effects for SiO₂ on a silicon substrate. These include lower concentrations of transition metal contaminants and of mobile ions, increased minority carrier lifetime in the silicon bulk, and improved oxide breakdown strength and lower interface trap densities of the film. Higher growth rates of chlorinated oxides can also be exploited to enhance the process throughput. Chlorinated oxides have also been recommended in advanced isolation schemes.

In the conventional approach, chlorine is introduced in the oxide by growing it in gas mixtures consisting of oxygen and small amounts of HCl or chlorine. Due to the high corrosive nature, flammability and extreme toxicity of Cl₂ and HCl, alternate, more benign chlorinating agents (mainly organic compounds containing chlorine) have been identified. In a so-called "point of use" generation scheme, HCl is externally generated close to the wafer process chamber by oxidizing vapors of the organic compound with O₂ in a heated environment. Following this step, HCl is transported to the wafer through stainless steel gas lines. Several organic precursors with low levels of ozone depletion potential have been synthesized for this application. Since these materials are usually liquids, they are stored in a bubbler and the vapors are transported to the reaction site using an inert carrier gas.

Even though RTP oxides have been shown to be superior to furnace oxides in several respects, further improvement through chlorination by either HCl or Cl₂ or organic precursors is difficult to implement in RTP due to the potential corrosion of the metal hardware (gas lines, flanges etc.) exposed to HCl or Cl₂. Transporting HCl from outside the chamber also requires suitable sensors, alarms and interlocking arrangements to prevent hazardous situations due to accidental leaks of the extremely toxic gases.

OBJECTS OF THE INVENTION

The object of the invention is to overcome the above described problems and make use of chlorine generation inside the RTP chamber. The method of this invention injects an organic halogen containing gas, preferably an organic precursor containing chlorine, directly into the RTP chamber so that reactive chlorine or a reactive chlorine compound is generated on the substrate surface from the dissociation of the organic precursor due to the temperature of the substrate. Therefore, reactions involving chlorine occur only on the hot wafer surface. Since reactive halogen products are generated only over the wafer surface and not outside the chamber, none of the metal hardware upstream of the wafer is exposed to any corrosive gases. Problems related to wafer contamination from corrosion of exposed metal parts are eliminated. The concentration of halogen products in the exhaust is small, as they are generated only over the wafer surface. The exhaust treatment requirements for safe operation are considerably reduced. No special storage or safety requirements related to gas transport are needed as the precursor is benign and non toxic.

SUMMARY OF THE INVENTION

The present invention is a system, apparatus and method to introduce organic halide compounds, most preferably chlorine compounds, directly into the processing chamber of a Rapid Thermal Processing (RTP) system, and subsequently to rapidly raise the temperature of a wafer being processed to a temperature high enough to dissociate the organic halide. The reactive halogen or halogen compound formed may then react with the material of the surface to incorporate the halogen into the surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an illustration of a Rapid Thermal Processing system with apparatus for performing the method of the invention.

Fig. 2 is a flow chart showing the steps of the most preferred method of the invention.

Fig. 3 shows film growth curves of a 900C° process.

Fig. 4 shows film growth curves of a 950C° process.

Fig. 5 shows chlorine profiles of 3.4nm thick oxide grown at 900C°.

Fig. 6 shows carbon profiles of 3.4nm thick oxide grown at 900C°.

Fig. 7 shows interface trap density for 3.4nm thick oxide.

Fig. 8 shows flat band voltage of 3.4nm thick oxide.

Fig. 9 shows charge trapping characteristics of 3.4nm thick oxide.

Fig. 10 shows leakage currents of various of 3.4nm thick oxides.

DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 shows an RTP processing system with attached apparatus for practicing the method of the invention. A semiconductor wafer 110 to be processed is supported in a quartz RTP chamber 120 by quartz support pins 160 (only one shown). A guard ring 170 is used to lessen edge effects of radiation from the edge of the wafer 110. An end plate 190 seals to the chamber 120, and a door 180 which can be sealed to end plate 190 allows entry of the wafer 110. Process gases flow through the chamber by entering opening 125 and exiting (not shown) at the opposite side of the chamber to opening 125. Two banks of radiation sources 130 and 140 are shown on either side of the wafer 110. Radiation sources 130 and 140 are typically quartz halogen lamps which produce visible and near infrared light which heat the semiconductor wafer 110. A computer 175 or other control means as are known in the art is used to control the lamps 130 and 140, to control a gas flow controller 185, and to control and receive measurements from the temperature measuring system, denoted here as a pyrometer 165. The particular details of the depicted and described RTP system are not central to the present invention. For anyone skilled in the art it must be clear that many variations on the presently described RTP system are possible. RTP systems are well known in the art and are under constant evolution. The apparatus for carrying out the method of the invention is a bubbler 135 holding a liquid organic halogen compound 145. An inert gas 155 such as nitrogen flows through the bubbler, and picks up a concentration of the organic halogen compound as a gas. Other gas lines may be used to introduce into the chamber of the RTP system other inert gases 146 (such as nitrogen or argon or other inert gases as known in the RTP art) and other reactive gases 147 (such as oxygen, silane,

or other reactive gases as known in the RTP art). The gas streams are mixed before or just after entry into the RTP chamber.

Fig. 2 shows a flow chart of the method of the invention. A semiconductor wafer is placed into a rapid thermal process chamber in step 202. In the most preferred embodiment of the invention, the wafer is a silicon wafer. Alternatively, the wafer can have a surface which is a silicon-on-insulator (SOI) surface, or the surface layer can comprise a certain percentage of germanium. Alternatively, the wafer may have a surface comprising a III-V material such as gallium arsenide or gallium nitride or a II-VI material such as ZnSe. The wafer may be cleaned by dipping in dilute HF, and then the wafer be transferred from the HF dip into the process chamber rapidly enough that the silicon surface is passivated by fluorine atoms and hence no native oxide grows on the silicon surface during the transfer. In some embodiments, a thin layer of well controlled oxide remains on the wafer as it is inserted into the chamber. It is preferable that the RTP system be pumped down and flushed with inert gases possibly multiple times, according to known steps in the art, such that the substrate rests in a clean inert environment. In step 204 the temperature of the substrate is stabilized at a relatively low temperature. This temperature can be the ambient room temperature, or preferably a slightly elevated temperature to give optimal conditions for introducing gas and vapor flows. However, the stabilization temperature is significantly below the temperature where any of the halogen compound to be introduced would react on the surface. Thus, the stabilized temperature is typically below 300°C, and preferably below 100°C. At this point, in step 206, the flow of a halogen containing organics gases is started. The preferred halogen is chlorine and the preferred organic precursor is trans-1,2-dichloroethylene (trans DCE). Other preferred gases are 1,1,1-trichloroethane (TCE) and oxalyl chloride. These organic precursors are liquids at room temperature. The organic precursor is housed in the bubbler 135 and the vapors are transported to the reaction site using an inert carrier gas, preferably nitrogen (N₂). Although the reaction rate of the chlorine produced in the chamber can be controlled by varying both the liquid temperature and the carrier gas flow, for simplicity the bubbler is preferably maintained at room temperature and the carrier gas flow (nitrogen) is regulated. Additional gas introductions, if any, in step 206 vary, depending on the type of film growth that is desired. In an embodiment of the invention, a wafer with a preexisting oxide is treated with the organic chloride vapor. The vapor decomposes on the hot surface of the wafer, and the chlorine reacts with the surface and chlorinates the surface. Carbon is deposited

on the hot surface as a byproduct of the reaction, and can be removed in a later step by heating the wafer in an oxygen atmosphere. If the wafer temperature is sufficiently low when the carbon is removed, the oxide thickness does not increase significantly. In the case that the temperature is raised to oxide growth temperatures, the chlorine produced on the surface is buried as further oxide grows. In the most preferred embodiment of the invention a chlorinated oxide film is produced, and this particular species will be described below. However, this is not to be regarded as limitation, as one skilled in the art can recognize the different possibilities that the dissociation of a halide into a reactive form on the wafer surface represents in semiconductor wafer processing.

In the most preferred embodiment, an oxide is grown in the presence of chlorine or a chlorine compound produced from the organic chlorine compound. Oxygen (O_2) flow is commenced, as well, in step 206. If sufficient oxygen flows simultaneously with the organic precursor, there is no carbon deposition. The oxide film also grows faster with the chlorine than it would without the chlorine. For electrical data measurements cited later, a carrier N_2 flow of 100 sccm through the bubbler was used, while for SIMS data, both 100 and 200 sccm flows were studied. An O_2 flow rate equal to at least the N_2 carrier gas flow rate was required to ensure good oxidation. For simplicity, the O_2 flow in all cases was maintained at 3 slm, which was much higher than the required minimum. Therefore, a 100 sccm flow rate of carrier gas was equivalent to using a lower Cl concentration on the surface and a carrier flow rate of 200 sccm corresponded to a higher Cl concentration on the surface.

In step 208 the power of radiation sources 130 and 140 is increased rapidly until substrate 110 reaches an optimal reaction temperature. As control is the essence of an RTP processing system, the temperature ramp-up was set at $50^\circ\text{C}/\text{sec}$, and reaction times at the stabilized reaction temperature are measured in seconds. The reaction temperature in step 210 is to be set to be above the dissociation temperature of the trans-1,2-dichloroethylene and in the range of rapid oxide growth. Since trans-1,2-dichloroethylene dissociates on the hot surface around 700°C , and oxide grows with the necessary speed approximately above 850°C , this latter temperature is the determining one. At 900°C trans-1,2-dichloroethylene is completely dissociated on the surface and the chlorine ready to react with any and all materials on the surface. With a growing oxide present the chlorine freed at the surface incorporates itself into the oxide, resulting in the desired chlorinated oxide film. Most preferred conditions are for temperatures between 900 and 950°C .

and for reaction times between 2 and 20 seconds. Following the reactions the radiation power is decreased and the wafer 110 is allowed to cool approximately at the rate of $50^{\circ}\text{C}/\text{sec}$ in step 212. After the cool down still in step 212 the RTP system is flushed with an inert gas, like nitrogen, and the wafer is removed. The thermal budget for the oxidation process could be as low as 3 seconds at 950°C or 14 seconds at 900°C . Higher temperatures of 1000, 1050, and 1100°C may be used for faster growth rates or thicker oxides.

The figures described below illustrate extensive measurements that were carried out on the grown oxide which show that the electrical properties are superior to oxides grown by different methods. Figs. 3 and 4 show growth rates for different oxidation conditions at 900 and 950°C respectively. In both cases, a clear increase in oxidation rates is observed whenever Cl is used. From a practical standpoint, the data in Figs. 3 and 4 illustrate that a broader range of oxide thickness can be grown with Cl, thereby extending the range of applications for RTP. It is interesting to note that using the higher concentration of Cl used does not provide any significant increase of growth rates over the lower one.

Figs. 5 and 6 show the SIMS generated plots of chlorine and carbon profiles respectively for the 34 Å oxide grown at 900°C for the two concentrations of Cl. Fig. 5 shows uniform chlorine distribution for both chlorinated oxides. It is interesting to observe that using higher Cl concentration leads to only a marginal increase in incorporated chlorine over a lower one, thereby suggesting that saturation is reached in between these concentrations. Figure 6 illustrates that carbon incorporation tends to reduce with *in-situ* chlorination.

Reduction of interface trap density (D_{it}) through chlorination is one of the principal advantages of chlorinated oxides. As shown in Fig. 7 in all cases, the values of (D_{it}) were found to be reasonable for samples that did not go through any forming gas annealing.

Fig. 8 summarizes the flat band voltages for the different oxides. The values are more negative for chlorinated oxides which suggests higher fixed charges. The effect is greater for the 900°C oxides. The fixed charge densities calculated from these data using documented work functions of mercury and p-Si range from 2.5×10^{12} to $3.5 \times 10^{12}/\text{cm}^2$.

Fig. 9 compares charge trapping data for the different oxides investigated. In all cases, it was observed that the threshold voltage became more positive after the current stress, indicating electron rather than hole trapping. This figure clearly shows that chlorination through *in-situ* generated Cl does not increase charge trapping over non chlorinated oxides. This indicates that

hydrogen incorporation in the chlorinated oxide, if any, is insignificant and does not modify the trapping characteristics of the oxide.

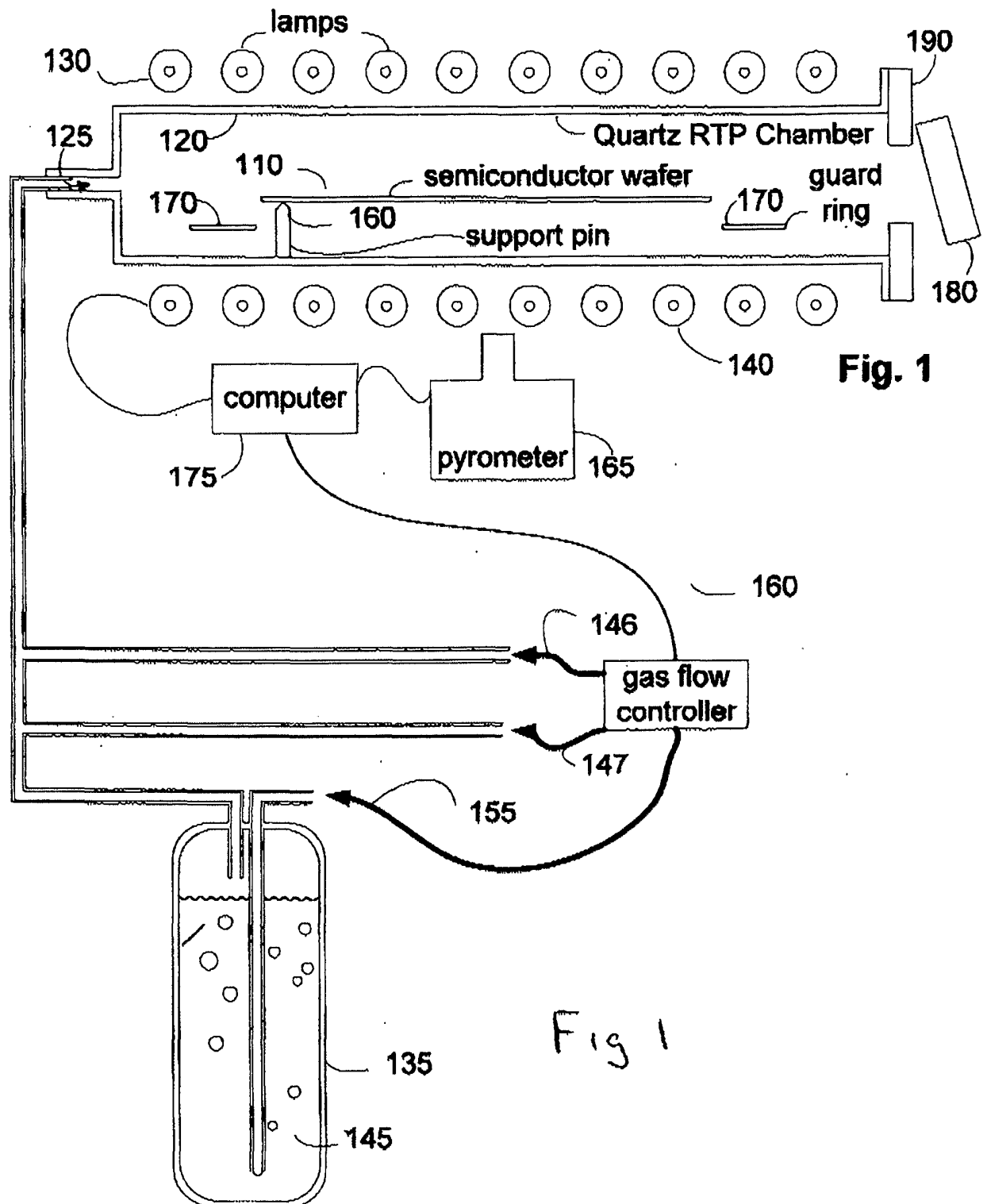
Fig. 10 compares leakage current densities of chlorinated and non-chlorinated oxides at 900 and 950°C. The values correspond to the mean of measurements taken at 20 points. The leakage current in this thickness regime can vary by more than an order of magnitude for small variation in oxide thickness. For instance, the leakage current at 2 V for a 35 Å oxide was reported to be 2 orders of magnitude higher than the value for a 30 Å oxide. Consequently, it is very difficult to establish any definite correlation between the growth condition and leakage current based on the small variations shown in Fig. 10. These results suggest that interface roughening with Cl grown oxides, if any, is insufficient to cause any drastic increase of leakage currents. It is also worth noting that all oxides show leakage current densities lower than the maximum values stipulated for gate oxides.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

WE CLAIM:

1. A method of processing a semiconductor substrate in a rapid thermal processing (RTP) system, comprising the steps of:
introducing a semiconductor substrate into a process chamber of the rapid thermal processing system;
contacting a surface of the substrate with an organic halogen containing gas; and
rapidly raising the temperature of the substrate to a temperature at which the halogen containing gas dissociates.
2. The method of claim 1 wherein the substrate surface comprises silicon.
3. The method of claim 2 wherein the organic halogen containing gas is a vapor of an organic precursor containing the halogen.
4. The method of claim 3 wherein the halogen is chlorine.
5. The method of claim 4 wherein the temperature is greater than 700C°.
6. The method of claim 5 further comprising the step of introducing oxygen into the chamber.
7. The method of claim 6 further comprising the step of utilizing an inert carrier gas to carry the vapor of the organic precursor containing chlorine.
8. The method of claim 7 wherein the vapor of the organic precursor containing chlorine is obtained by bubbling the inert carrier gas through a liquid form of the vapor of the organic precursor containing chlorine in a bubbler outside the chamber.
9. The method of claim 8 wherein the concentration of gases on the surface of the substrate, is controlled by individually adjusting the flow rate of the various gases, and by setting the temperature of the liquid organic precursor containing chlorine in the bubbler.

10. The method of claim 9 wherein the flow rate of oxygen is at least equal to the flow rate of the inert carrier gas.
11. The method of claim 10 wherein the organic precursor containing chlorine is trans-1,2-dichloroethylene.
12. The method of claim 11 wherein the inert carrier gas is nitrogen.
13. The method of claim 6 wherein material on the surface of the substrate comprises silicon, oxygen, and chlorine (chlorinated oxide).
14. The method of claim 2 wherein substrate surface further comprises germanium.
15. A system for RTP of semiconductor wafers, comprising;
an RTP system; and
a bubbler attached to the RTP system, the bubbler containing an organic halogen containing compound.



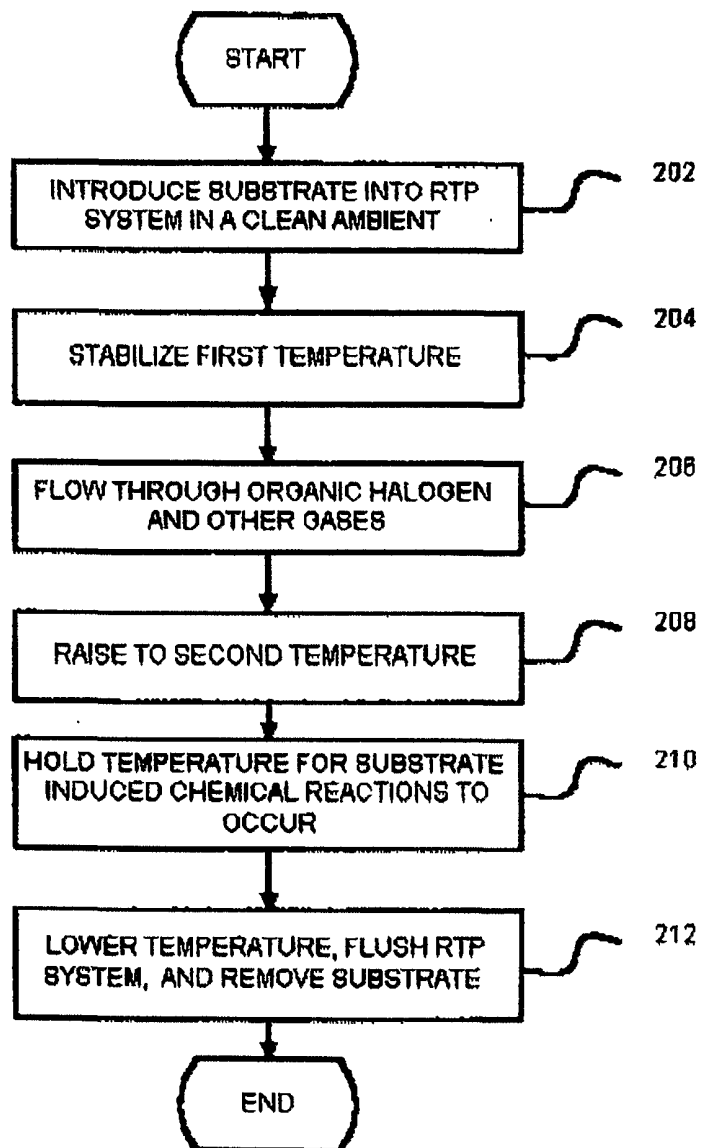
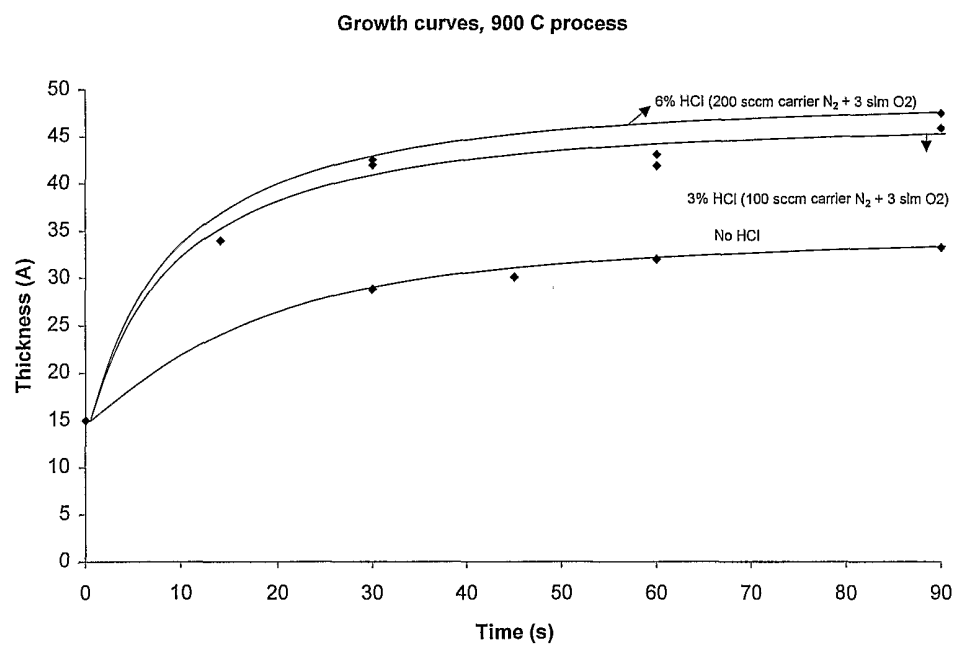


Figure 2

Fig. 3



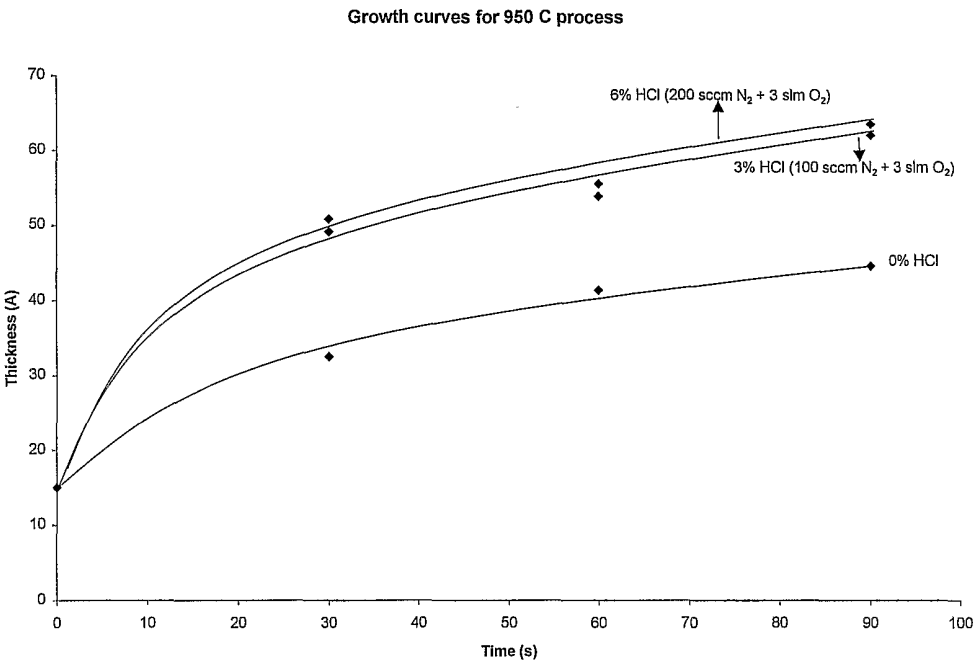


Fig. 4

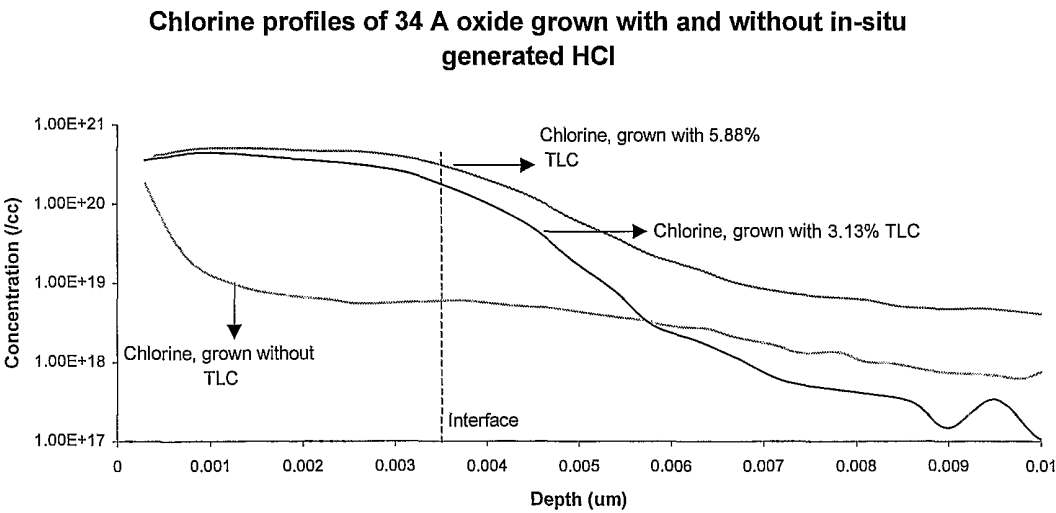


Fig. 5

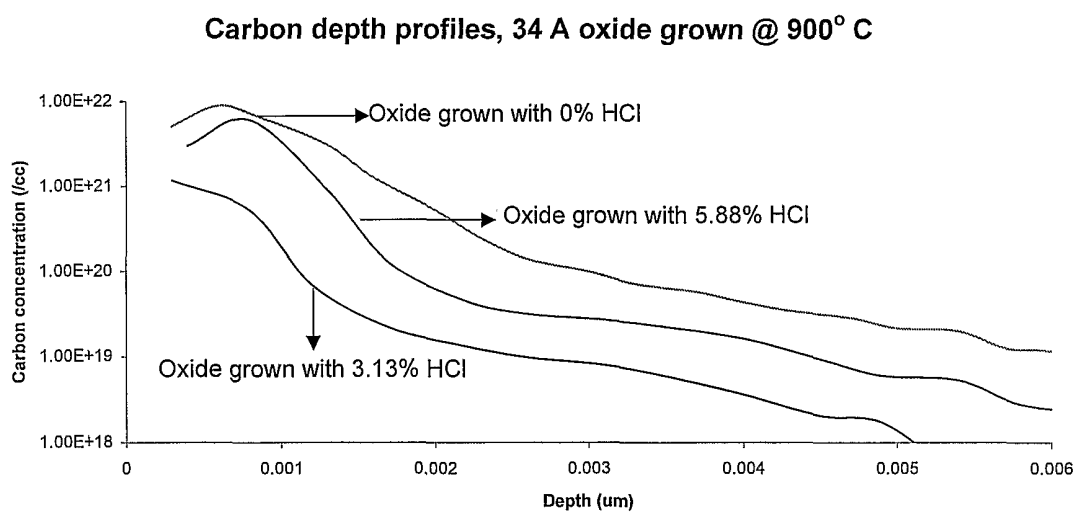


Fig. 6

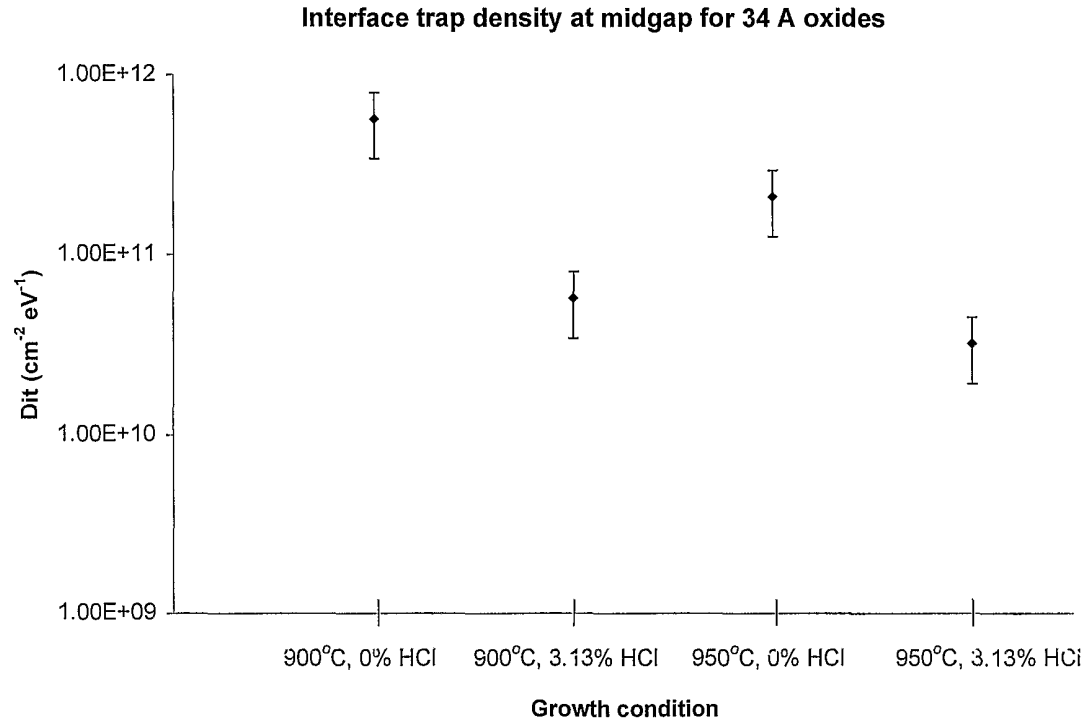


Fig. 7

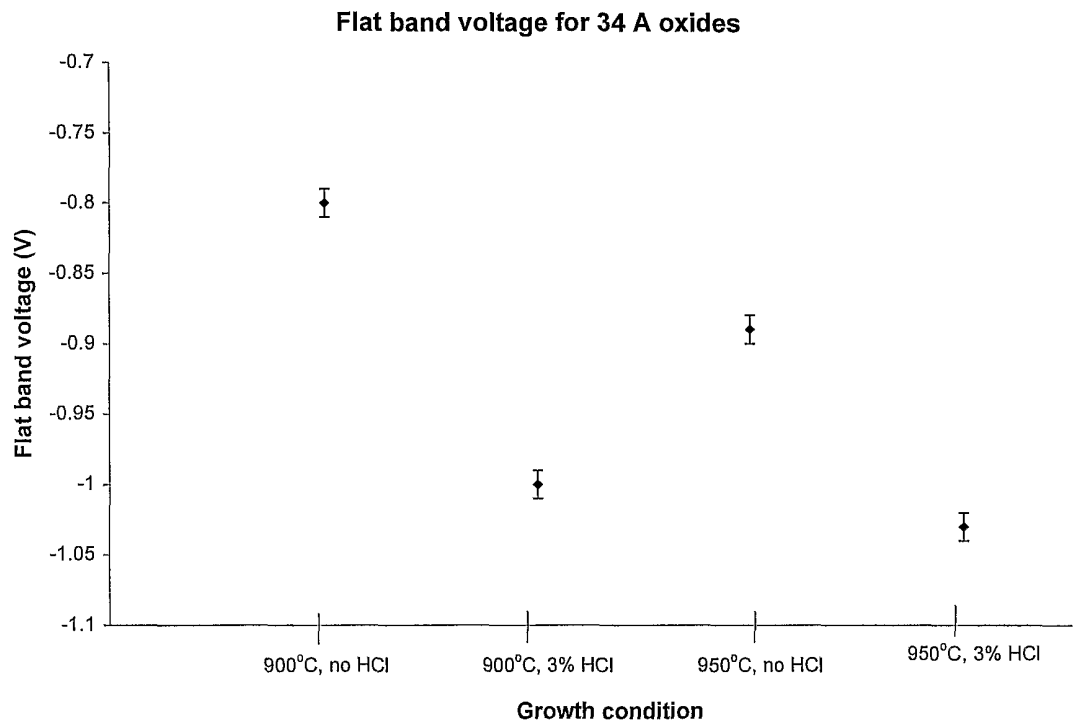


Fig. 8

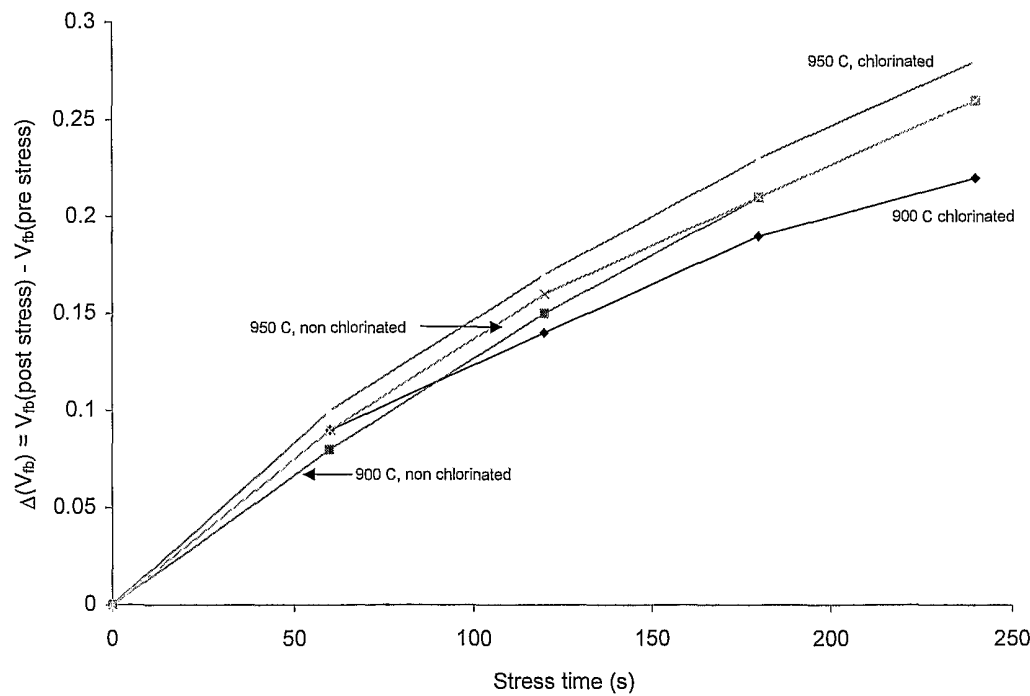


Fig. 9

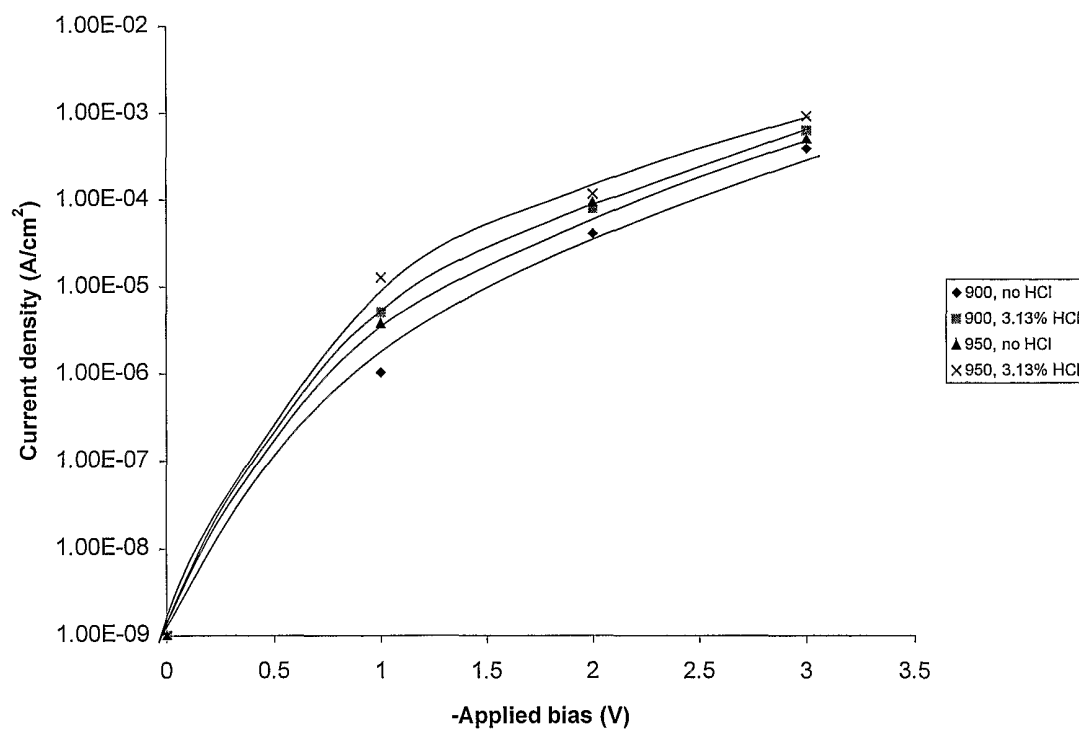


Fig. 10

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/IB 01/01229

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/28

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)

IPC 7 H01L

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

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

INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GLÜCK, M. ET AL: "Homogeneity of Wet Oxidation by RTP" MAT. RES. SOC. SYMP. PROCEEDINGS/RAPID THERMAL AND INTEGRATED PROCESSING III SYMPOSIUM, vol. 342, 4 - 7 April 1994, pages 215-225, XP001036655 San Francisco, CA - USA the whole document	15
A	EP 0 577 262 A (OLIN CORP) 5 January 1994 (1994-01-05) abstract	1-14
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

2 November 2001

Date of mailing of the international search report

19/11/2001

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 01/01229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 01/01229

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