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**U1S** S1421 S2061

(56) Documents Cited
**GB 2207809 A** **EP 0516344 A1** **EP 0337725 A2**
**WO 96/02939 A1** **WO 96/02938 A1** **US 5419787 A**
**US 5290731 A** **US 5136362 A**

(58) Field of Search
UK CL (Edition ) **C7B BBPJ BBPK BCCF BCCM , C7F FACE FACX FAHE FAHX FASE FASX FAXE FAXX FHB FHE FHX , H1K KHABX KHAX KJACX KLX**
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(54) **Filling recesses in a surface of a workpiece with conductive material**

(57) A method of filling recesses in a surface layer of a workpiece with conductive material includes the steps of:

forming a barrier layer on the surface;

depositing a layer of conductive material on to the barrier layer;

and forcing, flowing or drifting the conductive material into the recesses characterised in that the barrier layer includes Oxygen or is oxidised and oxidised material in the surface of the layer is nitrided prior to the deposition of the conductive material. The barrier layer may be based on titanium and the conductive layer may be aluminium, an aluminium alloy, copper or silver. The barrier layer may be formed by chemical vapour deposition and the conductive material layer by physical vapour deposition or electroplating.

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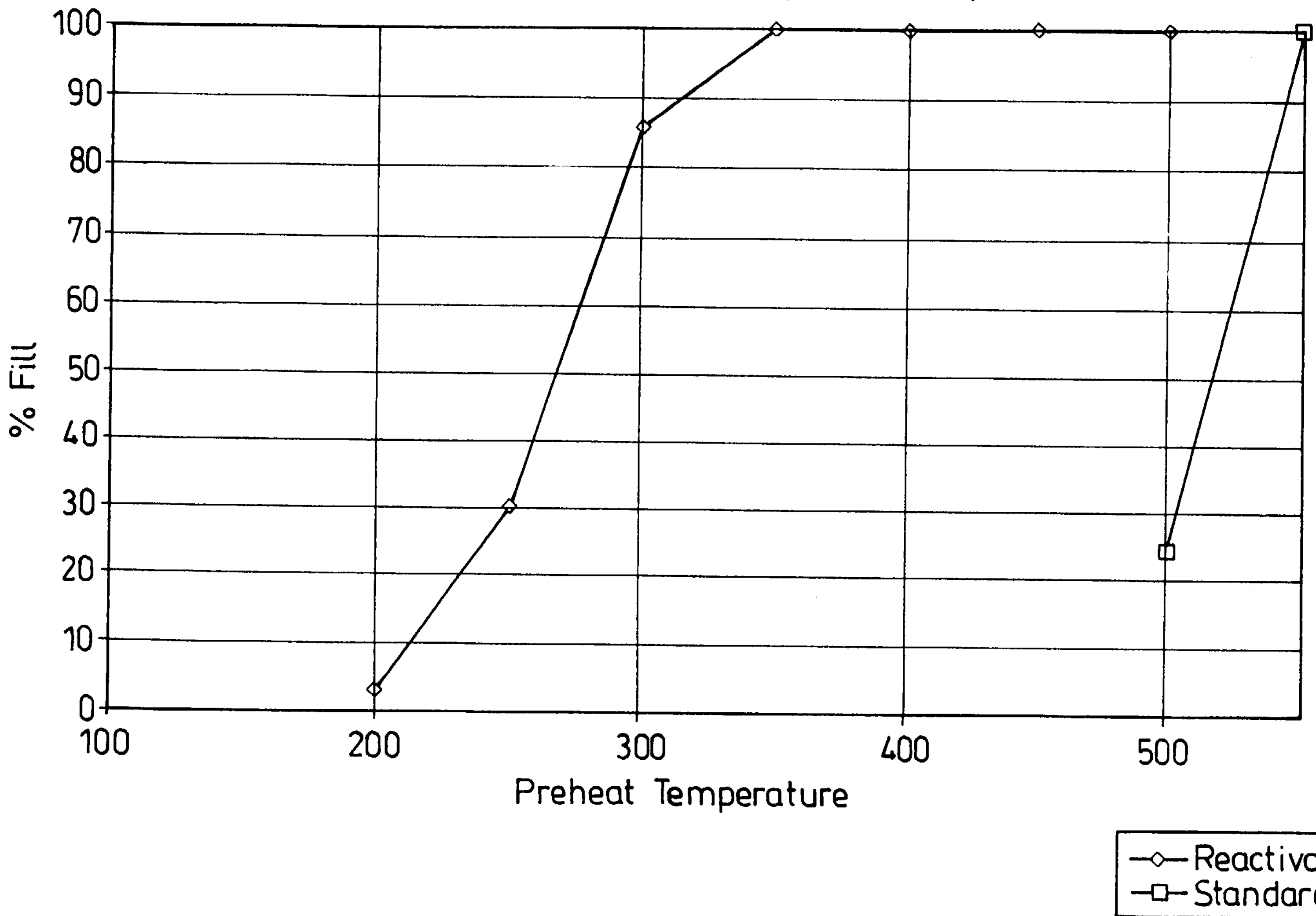
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.


Graph 1: % fill variation with preheat temperature with 460C fill processing
% Fill
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
Preheat Temperature
Reactivation after Ti/TiN
Standard Recipe

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Method and Apparatus for Treating a Semiconductor Wafer

This invention relates to methods and apparatus for treating a workpiece, such as a semiconductor wafer and, in particular but not exclusively, to methods and apparatus for providing a layer where there are recesses on the surface of the workpiece.

In our earlier co-pending European Patent Application No. 92304633.8 and British Patent Application No. 9619461.8 (the contents of which are incorporated herein by reference) we describe improvements to a method of at least partially filling recesses on the surface by means of the application of temperature and pressure. Other methods involve drifting molten metal into the recesses, e.g. by surface diffusion.

One of the main applications for such techniques is for the depositions of an interconnect layer that typically consists of several elements of which the main elements are:

(i) A barrier layer. This is frequently of Titanium or Titanium alloy and its purpose is generally to provide good adhesion to the surface layer and to avoid unintentional or undesirable alloying between the connection layer and the surface layer, in particular to avoid Aluminium alloy "spiking" through a contact junction.

(ii) A main conducting layer which is typically of Aluminium alloy. It is this layer that forms the bulk of the combined structure and the processes revealed in the above-mentioned

Applications describe how it is forced into recesses on the surface of the wafer by the application of heat and pressure such as to substantially fill the recesses.

(iii) A top layer of Anti-Reflection coating to aid
5 subsequent lithographic steps.

It should be understood that any or all of these elements can be deposited in separate pieces of equipment and the wafer is exposed to atmosphere as it is moved to the next. However, exposure to atmosphere causes the exposed
10 surface of the wafer (e.g. the barrier layer) to be modified e.g. by the formation of oxides. This may be considered desirable as in the case TiN, it seems to enhance the 'barrier' qualities of the layer.

However, it has been found that the recess filling
15 process disclosed in the co-pending Applications has failed to work reliably unless exposure of the TiN barrier layer to atmosphere is avoided or is negated.

The present invention consists in a method of filling recesses in a surface layer of a workpiece (e.g. a
20 semiconductor wafer) with a conductive material including the steps of: forming a barrier layer on the surface; depositing a layer of conductive material on to the barrier layer; and forcing and/or flowing the conductive layer into the recesses, characterised in that the barrier layer
25 includes Oxygen or is oxidised and oxidised material in the surface layer is nitrided prior to the deposition of the conductive layer.

For convenience, in this specification, the step set out in the characterising clause above will, on occasions, be referred to as "reactivation".

The barrier layer and the conductive layer can be deposited or formed in any suitable manner and can even be laid down as foil sheets. However, in a preferred embodiment, the barrier layer is formed in a first apparatus and the conductive layer is deposited in a second apparatus. The first apparatus may be chemical vapour deposition (CVD) apparatus, whilst the second apparatus may be physical vapour deposition (PVD) apparatus or electroplating apparatus. The ability to cope with the oxidation, which results from any vacuum break, means that the most preferred apparatus for forming or depositing any layer can be used. The conductive layer may preferably be formed of Aluminium, Aluminium alloy, Copper or silver.

The step of nitriding may be performed with a Nitrogen containing plasma. Additionally or alternatively, the barrier layer may be exposed to plasma-generated atomic Hydrogen in the presence of Nitrogen to nitride any oxidised material in the barrier layer. Alternatively the Oxygen stripping step by atomic Hydrogen and the nitriding step could be performed sequentially. With current apparatus, at least, nitriding in a pure Nitrogen atmosphere is difficult to achieve. The ratio of Hydrogen:Nitrogen may be between 1:10 and 3:1. The Hydrogen may be supplied in the form of $NH_3$, in which case the $NH_3$ may supply at least some of the nitriding Nitrogen.

It is believed that it is the presence of Oxygen that impacts recess filling capability and the thermodynamics of likely contamination chemistry indicates probable mechanisms and suggests solutions that have been found to be effective.

5 The barrier layer essentially contains atoms of Titanium and Nitrogen however Titanium Nitride forms columnar grain structures that present grain boundaries running from top to bottom. As the Titanium Nitride is acting as a physical barrier this is an inherent defect but 10 it is well known that it can be mitigated by the addition of Oxygen during the formation of Titanium Nitride, or the exposure of Titanium Nitride to Oxygen (e.g. through exposure to air). The Oxygen is said to "stuff" the grain boundaries.

15 It is thus preferential to have Oxygen additions to the Titanium nitride (to improve the barrier quality) however this presents a problem if the top surface contains some atomic Oxygen. Titanium and Nitrogen stably bond to form a TiN lattice. The subsequent recess filling process brings 20 Aluminium atoms into contact with the TiN surface. Under typical conditions the Aluminium is unlikely to bond to the top layer of Titanium and Nitrogen and so the Aluminium is free to flow into the recesses.

The effect of Oxygen contamination on TiN is that under 25 typical conditions there will be an oxidised surface, which consists of Oxygen atoms bonded to the outer layers of Titanium, which will come into intimate contact with the conductive material and under the typical process

conditions, which are required to flow conductive material into recesses, the conductive material is likely to form a chemical bond with the barrier layer thus inhibiting the flow of material. Obviously, the more reactive the conductive material, the more likely is the bond to form.

As has been set out above by the Applicants, it has been found that barrier layers containing Oxygen can be made suitable for subsequent processing by replacing at least the surface Oxygen atoms with Nitrogen.

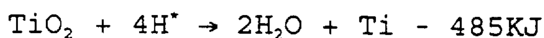
This has been achieved in a number of ways, in particular the use of Nitrogen and Hydrogen containing plasmas. An explanation of possible mechanisms is as follows.

The use of a Nitrogen containing plasma is probably explained by plasma generated species, possibly ion assisted, effectively nitriding the oxidised barrier surface.

$TiO_2 + N^* \rightarrow TiN + O_2$

This reaction is only slightly favourable above 625°C.

The use of a plasma - or Ultra Violet-generated atomic Hydrogen is more chemically favourable and does not require ion assistance:



$TiO_2 + 4H^* \rightarrow 2H_2O + Ti - 485KJ$

If this reaction is carried out in the presence of Nitrogen, the final barrier layer surface would be simultaneously nitrided.

The invention may be performed in various ways and specific embodiments will now be described, with reference to the accompanying drawing which is a plot of % hole fill against preheat temperature for standard filling and the
5 present invention respectively.

In the general process described on pages 1 and 2 above Chemical Vapour Deposited (CVD) is preferably used because TiN has superior characteristics than Physically Vapour Deposited (PVD) TiN. However, there can be a vacuum break as
10 the wafers are transported from the CVD equipment to the PVD equipment for the metallisation processes.

It is found that Aluminium alloys will not flow well into recesses over this TiN material due, it is believed, to a surface oxidation of the TiN. A subsequent PVD TiN layer
15 followed without vacuum break by the Aluminium alloy deposition is an effective solution, but is to be avoided because it leads to the mouths of the recesses being overhung by the subsequent barrier layer, thus inhibiting the filling of the recesses. A plasma process of the
20 following conditions has been found to modify the TiN surface sufficiently to enable good recess filling by the Aluminium alloy.

| | | |
|---|---|---|
| | $H_2/N_2$ ratio | 1:2 |
| | time | 2 minutes |
| 25 | typical pressure | 1100 millitorr |
| | Plasma Power | 300 watts |

This process yields:

| recess diameter | 0.5$\mu$m |
|---|---|
| percentage of recesses filled when the barrier layer is treated with a plasma process as above | 100% |
| without plasma process | 0% |

This process is effective but has not yet been optimised particular for smaller diameter recesses and is given by way of example only. It is believed that changing the ion characteristics, $H_2/N_2$ ratio, the Hydrogen source gas (e.g. $NH_3$), pressure temperature and other parameters will achieve 100% recess filling at all recess sizes down to at least 0.35$\mu$m.

Successful processing has also been achieved using the following conditions:

| | |
|---|---|
| Atomic Hydrogen/ Nitrogen ratio: | 3:1 |
| Pressure | >100 millitorr (eg.300-400 millitorr) |
| Applied plasma power | >500W, 13.56 MHZ (eg.1.2 KW) |
| Substrate temperature | 400~550 centigrade (eg.550°C) |

With $NH_3$ replacing the $N_2/H_2$ mixture complete fill of over 95% of 0.35 $\mu$m contacts was observed after the subsequent filling step. The process condition in brackets above have

achieved 100% for 0.35 μm contacts.

The oxidised Titanium at the surface is re-nitrided in the presence of atomic Hydrogen and atomic Nitrogen either from a mix of gasses or a single gas containing both Nitrogen and Hydrogen (and possibly other elements).
The re-nitridation by a mix of atomic Hydrogen and Nitrogen predominately takes place by an initial reduction of the Titanium oxide by the Hydrogen, and then a reaction of the Titanium with the Nitrogen.

Increasing temperatures increases the reaction speed probably by increasing the speed with which the water by-product of the reduction process leaves the substrate surface and so reducing the possibility of reoxidising the surface

$$TiN + 2H_2O \rightarrow TiO_2 + 1/2N_2 + 2H_2$$

At these temperature atomic Hydrogen is thus the enabling reaction as it make available Titanium to react with the Nitrogen. Therefore in a Nitrogen containing ambient atmosphere as atomic Hydrogen concentration is increased from zero the rate of conversion of Titanium Oxide to Nitride increases.

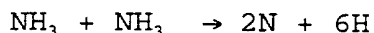
There will naturally come a point where the nitriding of the reduced Titanium Oxide becomes the rate limiting reaction as there are a fixed number of gas molecules in any given volume at constant temperature and pressure.

There is thus an optimum mix of atomic Hydrogen and Nitrogen for this process when carried out at temperatures less than that enabling a direct reaction of Titanium Oxide to Titanium Nitride in the presence of atomic Nitrogen.

The use of a gas molecule containing both Hydrogen and Nitrogen may be preferable to a mix of the two separate gases because more Hydrogen and Nitrogen atoms may be present in the fixed volume of gas at the substrate surface
5 being reacted.

By way of example in the same volume, when completely dissociated:

$N_2 + H_2 \rightarrow 2N + 2H$



$NH_3 + NH_3 \rightarrow 2N + 6H$

10 Further it is well known that in a plasma a Nitrogen containing gas such as Ammonia may be a much more ready source of atomic Nitrogen than molecular Nitrogen. It is also believed that $NH_3$ as a vapour will "stick" to the substrate more readily than Hydrogen or Nitrogen liberating
15 atomic Nitrogen and Hydrogen under energetic bombardment and thus promoting the required surface reactions.

An experimental result is that increasing molecular Nitrogen to Hydrogen gas concentrations up to 10:1 increases nitridation rates, yet this rate is still below that from
20 the use of Ammonia with its 1:3 Nitrogen to Hydrogen atomic content. This is probably because the atomic Nitrogen generated from the molecular Nitrogen is the rate limiting factor.

It has also been observed that as the concentration of
25 molecular Nitrogen in Hydrogen is increased still further

beyond a certain point the rate of nitridation reduces yet is still not at the same rate as that from a compound of Nitrogen and Hydrogen such as Ammonia. A possible explanation is that Titanium Oxide reduction is now the
5 limiting factor. Possibly the molecular Hydrogen has become so diluted in molecular Nitrogen that as atomic Hydrogen is formed it is physically precluded from reacting with the substrate surface as it is not in intimate enough contact with it due to the presence of a large number of (unreacted)
10 Nitrogen molecules.

In addition to the particular purposes to which nitriding is put in the method described above, it is believed that nitriding, for example as described above, a previously oxidised barrier layer, e.g. TiN, will improve
15 the barrier characteristics of the layer.

A further surprising advantage from the treatment of the barrier is that the preheat of the wafers need not be as hot.

Placing a workpiece previously in one gas ambient (e.g.
20 atmosphere) into a vacuum or another gaseous ambient causes the workpiece to "outgas" as gas and vapour leave the surface and enter the vacuum or new gas ambient.

This outgassing is particularly undesirable in plasma processes as they are carried out in a partial vacuum
25 consisting of a reduced pressure gas ambient chosen to be reactive in a specific way, or to be unreactive.

The lower the pressure of the process the more potentially deleterious the outgassing to the process as the outgassing will make up a greater proportion of the total

gas present or may make the low pressure unachievable without increasing the vacuum pumping speed or will require increased pumping speed and thus expense.

In particular sputtering processes are carried out
5 using an inert low pressure gas ambient typically argon. The argon gas is ionised in a flow discharge generally by applying a suitable negative voltage to an electrode thus providing a "feedstock" of ions which under the influence of the negative potential impact the electrode surface upon
10 which is placed a target material. Target material is sputtered away by ion impact through the argon plasma ambient and onto the workpiece placed conveniently nearby.

Argon is chosen because it is the most commercially attractive inert gas with a relatively massive ion.

15 However, if there are any potentially reactive gasses or vapour present in the argon ambient they will also be ionised by the glow discharge, becoming reactive and reacting with the sputtered material, either at the target surface, during the flight through the gas ambient or on
20 another surfaces.

When deliberately chosen this process is known as "reactive sputtering" and is used to sputter such materials as titanium nitride where nitrogen is added to the inert sputtering feedstock. However, when this occurs in an
25 uncontrolled manner, from the presence of water vapour, nitrogen, oxygen and the other constituents of atmosphere, then undesired oxides, nitrides and other materials are deposited or formed on the workpiece by reaction with the target material.

This is particularly undesirable for aluminium and its alloys because it increases resistivity and any inclusion of oxygen in the aluminium film will decrease the flowing properties of the aluminium into holes during the
5 application of pressure.

Therefore for sputtering processes outgassing is undesirable.

The main source of outgassing is the workpiece themselves as they are continually being placed into the
10 process chamber having previously been in atmosphere or other gas environment (e.g. dry nitrogen). Outgassing is a time consuming process and any speeding up of this process is desirable. Well-known ways of speeding up this process are heat and UV, heating being practically universally
15 employed. The greater the heat the faster the degassing.

However, wafers have a thermal budget and this use by preheating could be advantageously avoided.

What has been found is that wafers processed as set out above require lower preheating temperatures to obtain the
20 same hole filling results. In the experiments so far conducted, the process utilised an ammonia plasma.

It is not known exactly why this result is achieved but it cannot simply be as a result of plasma "conditioning", heating or energetic bombardment of the wafter surface
25 because in all cases the wafers are subjected to an argon (inert) plasma as part of the "sputter etch" process after preheating and prior to sputtering. The ammonia plasma process is in addition to and before the sputter etch process.

**Experiment A**

A large via chain array was used to establish the process limits. The vias were 0.4 μm wide and 1 μm deep. The different experimental splits were carried out on small wafer samples, processed on thermal oxide carrier wafers. The samples were then sectioned through the via array and analysed on the SEM. The fill capability of each process was determined by counting the total number of holes with complete hole fill and those which had voided. An average of 80-100 vias were observed per sample. The percentage fill was calculated for each sample.

**Results and Conclusion**

Preheat temperatures can be reduced from 550°C to 350°C if a nitriding step is included after Ti/TiN deposition. These temperatures are the minimum required to achieve 100% hole fill without and with the nitriding step respectively. The drawing shows how the hole fill capability increases with increased preheat temperature and how the nitriding process significantly reduces the minimum temperature required for complete fill. The lower preheat temperature will be more compatible for via processing as explained above. Reducing the process time to 2 minutes from the standard 4 minute contact will also help to improve throughput and reduce the length of time that the wafer is exposed to high temperature.

| Module | Standard Conditions | Reactivation Process Conditions |
| --- | --- | --- |
| Preheat | 1 Torr<br>550°C,3 mins | 350°C,3 mins,1 Torr |
| With nitriding | N/A | 350°C,2mins,1500sccm $NH_3$ 1200W platen power,560V DC bias |
| Standard filling | 460°C,1 min | 460°C,1min,1150bar inlet,700 bar chamber |

5 Comparing the minimum process requirements required for Ti via structures

## Claims

1. A method of filling recesses in a surface layer of a workpiece with conductive material including the steps of:

forming a barrier layer on the surface;

5 depositing a layer of conductive material on to the barrier layer;

and forcing, flowing or drifting the conductive material into the recesses characterised in that the barrier layer includes Oxygen or is oxidised and oxidised material 10 in the surface of the layer is nitrided prior to the deposition of the conductive material.

2. A method as claimed in Claim 1 wherein the barrier layer is formed in a first apparatus and the conductive layer is deposited in a second apparatus.

15 3. A method as claimed in Claim 2 wherein the first apparatus is Chemical Vapour Deposition (C.V.D.) apparatus.

4. A method as claimed in Claim 2 or Claim 3 wherein the second apparatus is Physical Vapour Deposition (PVD) apparatus or an electroplating apparatus.

20 5. A method as claimed in any one of the preceding claims wherein the step of nitriding is performed with a Nitrogen containing plasma.

6. A method as claimed in Claims 1 to 5 wherein the barrier layer is exposed to atomic Hydrogen prior to or 25 simultaneously with the nitriding step.

7. A method as claimed in any one of Claims 1 to 5 wherein

the barrier layer is exposed to plasma or U.V.generated atomic Hydrogen, in the presence of Nitrogen, to nitride any oxidised material in the barrier layer.

8. A method as claimed in Claims 6 or 7 wherein the
5 Hydrogen:Nitrogen ratio is between 1:20 and 3:1.

9. A method as claimed in Claims 6 or 7 wherein the Hydrogen is supplied in the form of $NH_3$.

10. A method as claimed in Claim 9 wherein $NH_3$ supplies at least some of the nitriding Nitrogen.

10 11. A method as claimed in any one of the preceding claims wherein the surface layer is preheated, subsequent to the forming of the barrier layer.

12. A method as claimed in Claim 11 wherein the wafer is pre-heated to approximately 350°C or below.

15 13. A method as claimed in any of the preceding claims wherein the conductive material is selected from the group: Aluminium, Aluminium alloy, Copper or Silver.

The Patent Office

17

**Application No:** GB 9724096.4
**Claims searched:** 1-13

**Examiner:** Peter Beddoe
**Date of search:** 28 January 1998

# Patents Act 1977
# Search Report under Section 17

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C7F (FHB, FHE, FHX, FACE, FACX, FAHE, FAHX, FASE, FASX, FAXE, FAXX); H1K (KHABX, KHAX, KJACX, KLX); C7B (BBPJ, BBPK, BCCF, BCCM)

Int Cl (Ed.6): C23C (8/34, 14/06, 14/58, 16/30, 16/56, 28/00); H01L (21/3105, 21/314, 21/321, 21/768); C25D (5/48, 5/50)

Other: Online: WPI

**Documents considered to be relevant:**

| Category | Identity of document and relevant passage | | Relevant to claims |
|---|---|---|---|
| Y | GB 2207809 A | (SAMSUNG) see esp p5 lines 6-21 | 1 at least |
| Y | EP 0516344 A1 | (ELECTROTECH) see whole doc | 1 at least |
| Y | EP 0337725 A2 | (FORD) see esp col13 line 35 - col14 line 5 | 1 at least |
| Y | WO 96/02939 A1 | (ELECTROTECH) see esp claim 1 & p10 lines 7-16 | 1 at least |
| Y | WO 96/02938 A1 | (ELECTROTECH) see esp claim1 1 | 1 at least |
| Y | US 5419787 | (LEVI) see esp col2 line 31 - col3 line 30 | 1 at least |
| Y | US 5290731 | (SONY) see esp exs | 1 at least |
| Y | US 5136362 | (GRIEF) see esp col11 lines 45-55 | 1 at least |

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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E Patent document published on or after, but with priority date earlier than, the filing date of this application.