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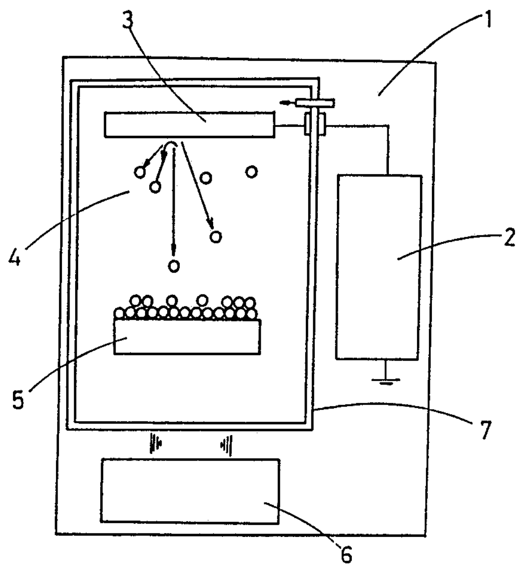
(54) Title: EXOTHERMIC REFLEXIBLE GLASS, EXOTHERMIC TRANSPARENT GLASS AN) PROCESS OF MANUFACTURING THEM



(57) Abstract

The present invention relates to a process of manufacturing an exothermic reflexible glass which can emit heat of over 50 °C by coating the matrix glass with a thin layer of such metals as Cr, Ni, Au, Ag, Al, Cu by use of the sputtering technique for plasma, and a process of manufacturing an exothermic transparent glass whose surface temperature can be adjusted to a desired degree by means of connecting to a power source, after coating the matrix glass with a thin layer of transparent material of indium-tin oxide by use of the reactive sputtering technique and also to the glass produced respectively by these processes.

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Exothermic Reflexible Glass, Exothermic Transparent Glass and Process of manufacturing them

BACKGROUND OF THE INVENTION

Field of Invention

This invention relates to the exothermic reflexible glass and exothermic transparent glass as well as to a process for the manufacture of them, whose surface temperature can be adjusted at will by means of coating non-conductive glass either with reflexibility-conductive material or transparency-conductive material by use of the sputtering technique generally used for plasma.

Description of Prior Art

The technique of vacuum evaporation by sputtering, the very technique of manufacturing exothermic reflexible glass and exothermic transparent glass here, is performed by a direct evaporation of the material to be evaporated in vacuum through colliding ionized inert gas into the surface of the target, that is, ionization of the inert gas takes place in the area of abnormal glow discharge and the thus ionized gas, under the influence of the electric field, is made to beat the surface of a cathode. Thus, in the sputtering technique, the target is used as the cathode and the vacuum container or the matrix, as the anode.

A simplest diode planar sputtering technique is shown in Fig. 1, wherein a low pressure electric discharge takes place between the target(3), which is used as the cathode, and the anode. The pressure of the inert gas in common use should, for the purpose of maintaining electric discharge, be over 5×10^{-3} torr, the working pressure ranging from 2×10^{-2} torr to 10^{-1} torr. The electric pressure applicable to the cathode can be varied from hundreds of volts to thousands of volts, while the distance between the cathode and the matrix(vacuum container), the anode, is so near as about 5cm. The velocity of vacuum evaporation being about 100Å/min, it is decided according to the energy and quantity of the ion being shot out. That is, the velocity of vacuum evaporation can be increased by raising the electric pressure and restricted by the decrease of the ionized cross section.

However, even though the ionized electric current can be increased by added pressure of inert gas, the velocity of vacuum evaporation can rather be decreased in an effect of dispersion of the gas. Thus, the optimum condition as to the velocity of the vacuum evaporation will have to be determined only through repeated experiments.

To see the basic idea of the sputtering it is known that when a certain pressure and electric tension are applied to a target(3), which exists within a vacuum container, plasma(4) is given rise to around the target and the positive ions existing in the area of the electric discharge come to beat the surface of the target by virtue of electric forces. At this time the kinetic energy of the positive ions is transferred to the atoms which exist on the surface of target, and if this energy is stronger than the bonding energy of the atom which are beaten, the atoms of the target are emitted.

The disadvantage of the sputtering technique lies in the very slow velocity in the coating formation, and the resultant low productivity, when a diode process is adopted. To solve the above problems the triode system has been invented, which has a third electrode for control of both the source of thermion emission, and the flow of the emitted thermion is added to the diode system, where a tungsten filament is used as the source of emission for the thermions.

When a triode system is adopted the velocity of vacuum evaporation can be increased, because it is possible to increase the concentration of plasma by the emission of thermions. When the concentration of the electrons in plasma is increased by emission of thermions, the probability of ionization is heightened by brisk action of electrons, the number of ions that beat the target is increased, and thus the velocity of vacuum evaporation is accelerated.

Besides the way of increasing the concentration of the plasma by supplying electrons there is another way of increasing the probability of ionization, that is, by means of controlling the action of electrons with the use of magnetism. The sputtering with the use of magnetism results in N and S electrodes at the back of the target changing the action of electrons from rectilinear to spiral.

Thus the probability of electrons to hit neutral atoms and others under the same pressure increases as the distance of electrons' movement is increased, and by heightening the probability of ionization a greater velocity for vacuum evaporation is obtained. Fig. 2(A)(B) show the structure of the target, wherein the highest probability of ionization is to be seen at the point at which a line of magnetic force intersects another perpendicularly, showing a regional sputtering taking place forming a belt of high plasma concentration.

SUMMARY OF THE INVENTION

The present invention is intended to provide both the process of manufacturing exothermic reflexible glass by coating any such metals as Cr, Ni, Au, Ag, Al, Cu over the surface of glass by the technique of magnetic sputtering as given above, and the process of manufacturing exothermic transparent glass by creating a layer of oxidized coating with In(90%)-Sn(10%) alloy in a vacuum container.

Also the present invention is intended to provide both exothermic reflexible glass and exothermic transparent glass prepared by the above processes.

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sketch of the diode planar sputtering apparatus of the present invention.

Fig. 2(A) and (B) are sketches to show the structure of a target for the sputtering.

Fig. 3 is a graph showing the different transparencies of the respective ITO and Au thin coating test pieces on glass of different times spent on vacuum evaporation.

Fig. 4 is a graph showing the different resistivilities of the respective ITO and Au thin coating test pieces of different times spent on vacuum evaporation.

Figs. 5(A) and (B) are graphs showing the surface temperatures of ITO and Au thin coatings of 6,000Å and 400Å thicknesses, respectively.

Fig. 6 shows results of the XRD analysis of ITO test piece whose F_{O_2}/F_{Ar} value is 0.43.

Indices

1....gas inlet, 2....power source,

3....target, 4....plasma,

5,11....substrate, 6....pumping system,

7....chamber, 12....electron,

13....argon, 14....atom sputtered,

15....target, 16....anode,

17....cathode, 18....magnetic field lines, 19....substrate carrier.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention the direct current supplied by the DC power supply source was used and, as shown in Fig. 2, magnetron was attached to the back of the target to raise the velocity of vacuum evaporation up to 1,000Å/min.

For the target an experimental item of 75mm in diameter and 5mm in thickness was used, and in the case of Ni a thin coating was formed on the target whose thickness was adjusted to 1mm - 1.5mm due to its propensity for magnetizing by magnetrons.

In the case of such metals as Cr, Ni, and Cu the density of the electric power applied to them is 11.3W/cm^3, and at the initial vacuity of 1 X 10^{-5} torr Ar gas of purity 99.995% was introduced for generation of plasma at the working pressure of 6 X 10^{-3} torr to produce reflexible glass. In the case of such metals as Au, Ag, and Al the density of the electric power was lowered to 6.8W/cm^3 because under same conditions, the velocity of vacuum evaporation of these is greater than that of Cr, Ni, or Cu.

The glass used as the matrix was 2mm thick, of 130mm respectively in length and breadth. It was placed under a process of cleansing with alcohol, distilled water, and aceton in that order, drying in an oven of 200℃ for 10 minutes and putting inside the sputter chamber, and then over 1,000Å thick coating was formed over its surface by the sputtering process. Then, when electric wires were attached by silver paste to the reflexible glass made by the above method electric power of about 0.06W/cm^3 was supplied, it was found that a temperature of over 50℃ was obtained on the density of the electric power and a desired temperature on the surface was obtained without difficulty.

Exothermic transparent glass is, unlike exothermic reflexible glass, made by coating glass with transparent oxide instead of using any single metal, and in the present invention a target of In(90%)-Sn(10%) was used for production of exothermic transparent glass, and indium-tin oxide(ITO) was synthesized under the mixture of Ar and O_2 for formation of the oxide. The specific feature of this material is that even when its thickness is 1,000Å it can allow penetration of light by more than 80% so that it can be made wide use of in production of the liquid crystal for TV or other liquid crystal display systems. Hence the extensive study of this material has been made recently.

Then indium-tin oxide(ITO) in the present invention is made through the reactional process of DC magnetron, and what is important at this time is the ratio of Ar and O_2 gas in the mixture. If the ratio of O_2 is lower than the preferable ratio, the desired oxide is not produced, while if it is higher than that, the transparency decreases and the transparent conductive coating is not obtained. Thereupon in the present invention, using a mass flow meter manufactured by a US company MKS, the flow of Ar gas was adjusted to 100 SCCM and the flow of O_2 gas to 30-98 SCCM, resulting in formation of a transparent conductive material of good quality, while setting the flow of Ar gas at 100 SCCM and O_2 gas at 43 SCCM is more preferable.

The density of the electric power can be 1.5 - 8.0W/cm^3 and if it is higher, it takes short time for the vacuum evaporation and if it is lower, it takes long time for it. It is more desirable to set the density of the power at 2.26W/cm^3 and the time at 6.5 minutes.

The experimental conditions for said indium-tin oxide(ITO) are given in Table 1 below:

TABLE 1. Experimental Conditions for ITO Vacuum Evaporation

Coating material	Process	Parameter
ITO	Reactive sputtering	Power density : 1.5 - 8.0W/cm^3 Working pressure : 6 X 10^{-3} mbar Sputtering time : 0.5, 1, 2, 3, 4, 5, 6.5, 8, 10, 12.5, 15 and 20 minutes FO_2/FAr = 0, 0.35, 0.43, 0.5, 0.7, 0.92, 0.98

The greatest factor that affects the transparency and conductivity at the time of production of the ITO thin coating is the partial pressure of O_2, and when the flow of the neutral Ar gas supplied for reactive sputtering was indicated by FAr and that of O_2 by FO_2, when the value of FO_2/FAr was 0.39 or lower a coating of very good conductivity but of very bad transparency was formed, while when the value was 0.45 or more the transparency was fine but the conductivity fell to MΩ /cm(megaΩ/cm). When the value of FO_2/FAr was 0.43 it was possible to form a coating fitting the purpose of the present invention, and the velocity of the formation of the coating at the time was measured about 1,200Å/min.

Among the materials which have so far been widely used in production of thin coating layers is Au with the best conductivity, and in the present invention Au was vacuum evaporated on glass by the sputtering technique in order to compare it with an ITO thin coating layer, when the speed of the formation of the coating was set at 40Å/sec. With Cr, Al, Ni, and Cu coating it was found practically impossible to produce a thin coating of such conductivity and transparency as will justify commercial production, but yet it was also possible to use them in production of conductive reflexible glass by means of increasing the tickness of the coating layers.

Fig. 3 is a graph to show the different transparencies of the ITO and Au thin coating layers obtained by varied times of vacuum evaporation. In the case of the ITO thin coating layer the penetration of light was about 80% when the thin coating layer's thickness was 0.8μm(vacuum evaporation by sputtering for 6.5 minutes), and the transparency gradually decreased as the layer's thickness increased, falling to 40% when the thickness was about 2.4μm(vacuum evaporation by sputtering for 20 minutes). On the contrary, in the case of the thin coating layer of Au, the transparency measured 65% with the thickness 200Å(vacuum evaporation by the sputtering for 5 seconds) and as the time for the vacuum evaporation increased the transparency rapidly fell.

The resistive features were measured by calculating the current, as 10V electric pressure was applied, after placing a Cu electrode each on both ends of an experimental piece of 72mm by 23mm size. Those showing resistance by MΩ units were measured with ordinary multi meters, the results being shown in Fig. 4. Fig. 4(A) carries a graph showing the resistive features of an ITO experimental piece, different as the time for vacuum evaporation by the sputtering varied. The value of resistance was 400Ω when the time for vacuum evaporation by the sputtering was two minutes, but it declined rapidly as the time was protracted to fall, for instance, as low as about 20Ω when the time was 10 minutes(1.2μm).

Fig. 4(B) carries a graph of the resistive features in the case of an Au coating layer, and in this, too, as in the case of the ITO coating layer, the resistance rapidly declined with rapidity as the time for vacuum evaporation by the sputtering increased.

The object of the present invention is to develop a material as well as the software for the manufacture of conductive and transparent glass for use in automobiles, and since the change of temperatures of the experimental piece makes, as well as its transparency, a most important part of the present invention, the temperatures should be measured acculately. Hence, on the surface of the experimental piece a K-type thermo-electric band was attached by means of silver paste and it was connected to a X-Y recorder in order to measure continuously the temperatures of the surface of the experimental piece varying at the change of the electric pressure and the electric current.

Fig. 5(A) is a graph showing the measured surface temperatures of the ITO thin coating layers of 6,000Å in thickness, drawing a curve of (a), (b), (c), (d), and (e) for 0.775W(5V X 0.155A), 1.512W(7V X 0.216A), 2.466W(9V X 0.274A), 3.3W(11V X 0.330A), 5.07W(13V X 0.390A), respectively. Moreover, the ITO thin coating of 6,000Å having, as shown in Fig. 3, a transparency of 80%, it can be adopted as a very important material in production of the conductive glass for automobiles.

Fig. 5(B) shows the curve indicating the surface temperatures of the Au thin coating layers of 400Å in thickness, the electric current being 0.114A when it was supplied at 13.8V, the surface temperature showing about 45℃ 600 seconds later.

Fig. 6 shows the results of XRD analysis of the ITO experimental piece with its FO_2/FAr value at 0.43, wherein in the case of an experimental piece of good transparency and conductivity its In_2SnO_5 coating exceedingly well develops at 2 θ = 45.36, and it was found that the above ITO coating contributed to improvement of conductivity.

Such exothermic reflexible glass, coated over the surface of the glass in automobiles, can be used very preferably to remove the moisture inside, and is extensively made use of for liquid crystal display systems also.

CLAIMS

1. A process of manufacturing an exothermic reflexible glass by the magnetic sputtering technique, characterized in that it is manufactured by cleansing glass with alcohol, distilled water, and aceton in that order, drying it in an oven at about 200℃ making it generate plasma in the magnetic filed of magnetron at the electric density of 6-12W/cm^3, the initial vacuity of 1 X 10^{-5} torr, and the working pressure of 6 X 10^{-3} torr, and coating it with such conductive metals as Cr, Ni, Ag, Al, Cu by sputtering to a thickness of about 1,000Å or more.

2. A process of manufacturing an exothermic transparent glass by the magnetic sputtering technique characterized in that it is manufactured by cleansing glass with alcohol, distilled water, and aceton in that order, drying it in an oven at about 200℃ making an alloy of In(90%)-Sn(10%) generate plasma in the magnetic field of magnetron, sputtering with the flow of Ar gas at 100 SCCM and that of O_2 gas at 30 - 98 SCCM, and forming an indium-tin oxide(ITO) thin coating layer over the glass under the initial vacuity of 1 X 10^{-6} torr and the working pressure of 6 X 10^{-3} torr.

3. A process of manufacturing an exothermic transparent glass according to Claim 2, characterized in that the flow of Ar gas is 100 SCCM and that of O_2 gas is 43 SCCM.

4. An exothermic reflexible glass manufactured by the process according to Clam 1.

5. An exothermic transparent glass manufactured by the process according to Claim 2.

FIG. 1

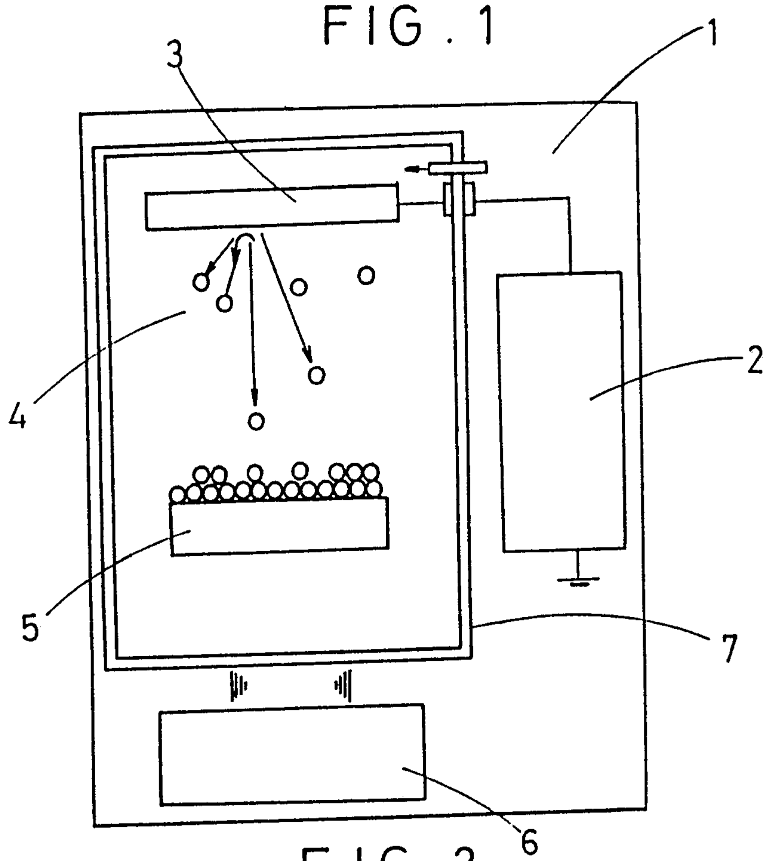


FIG. 2

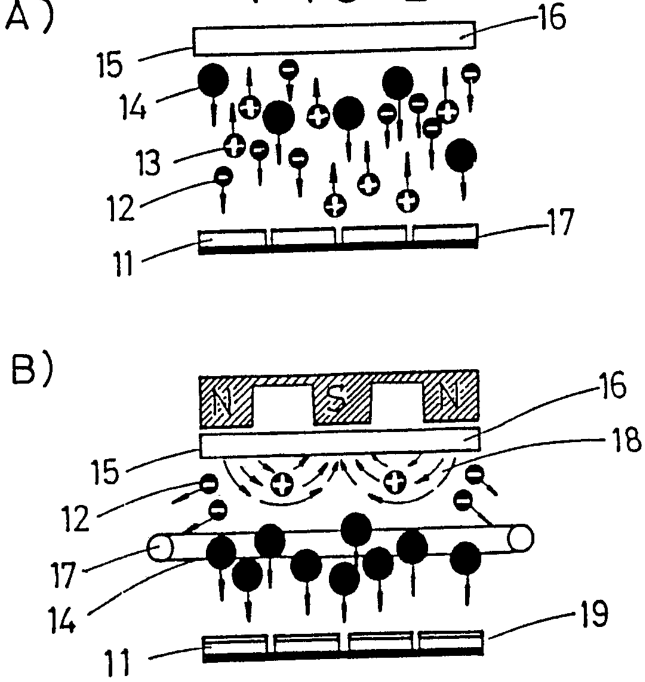


FIG. 3

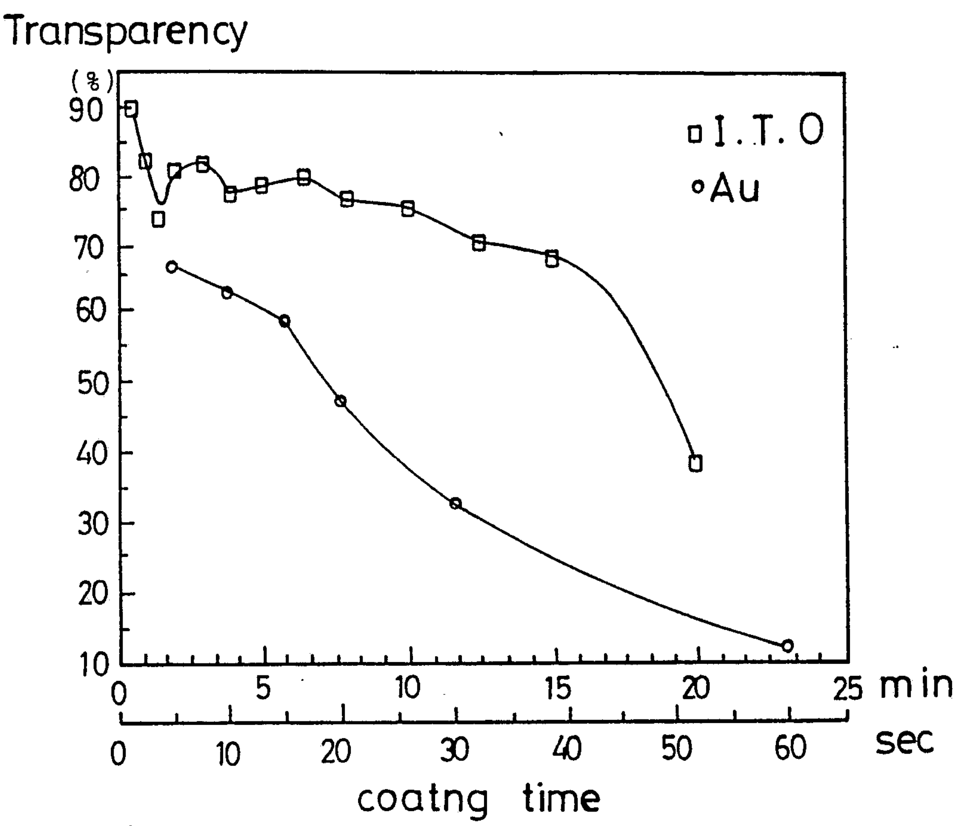
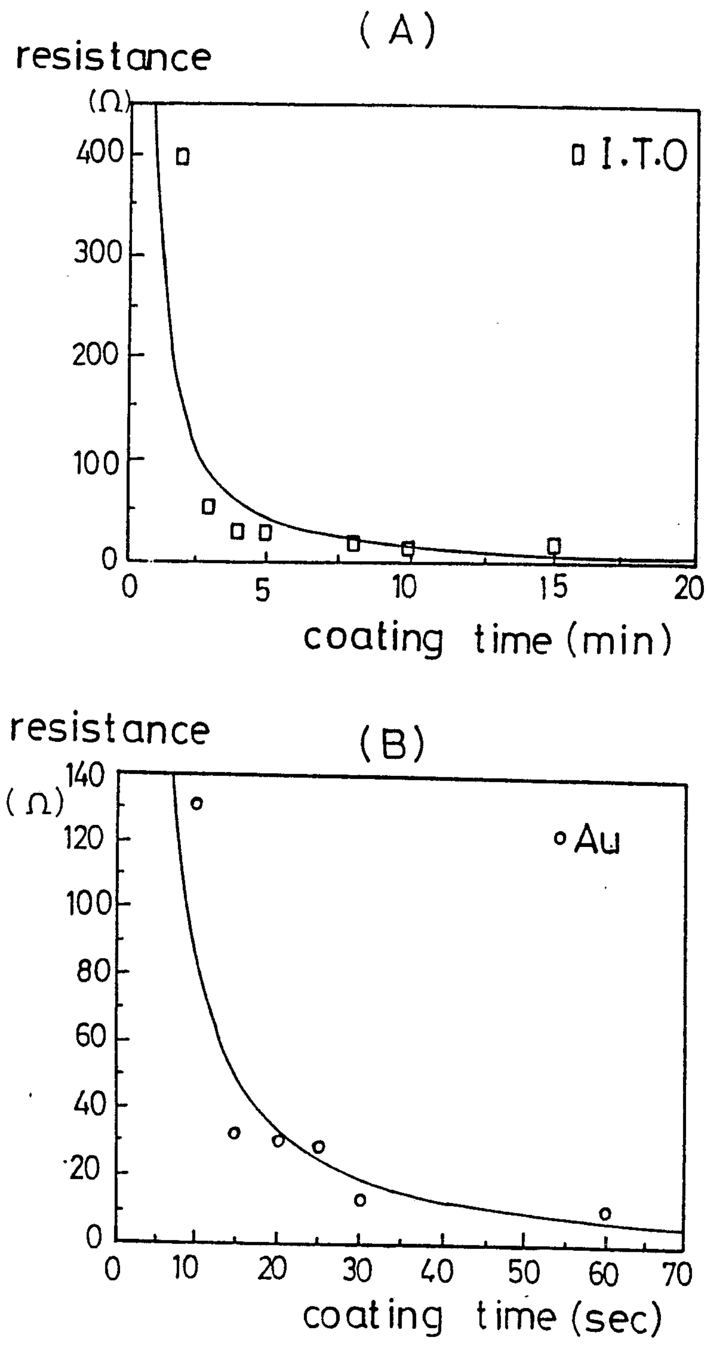

Transparency
(%)
90
80
70
60
50
40
30
20
10
□ I.T.O
○ Au
0
5
10
15
20
25
min
0
10
20
30
40
50
60
sec
coatng time

FIG. 4


(A)
resistance (Ω)
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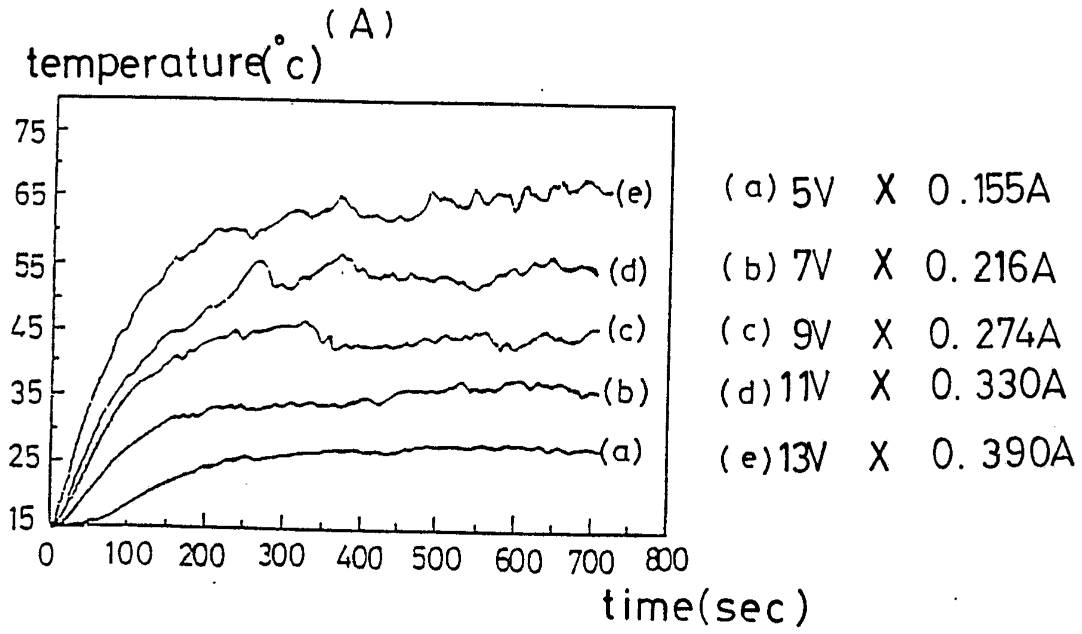
300
200
100
0
□ I.T.O
0
5
10
15
20
coating time (min)
resistance (Ω)
(B)
140
120
100
80
60
40
20
0
○ Au
0
10
20
30
40
50
60
70
coating time (sec)

FIG. 5


(A)
temperature(°c)
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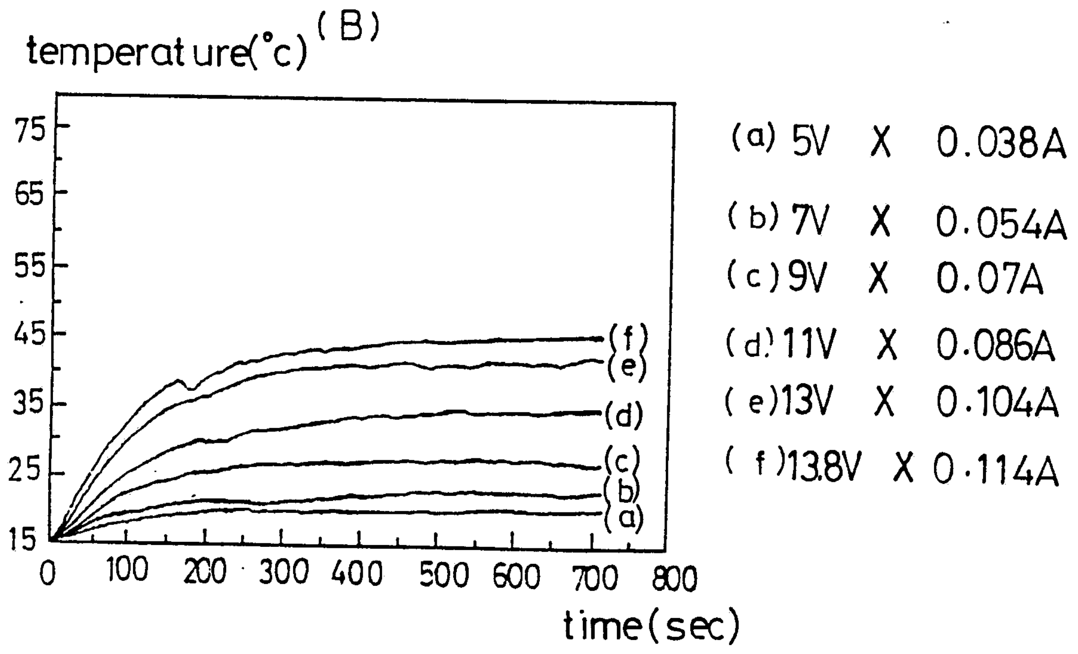
65
55
45
35
25
15
0 100 200 300 400 500 600 700 800
time(sec)
(e)
(d)
(c)
(b)
(a)
(a) 5V X 0.155A
(b) 7V X 0.216A
(c) 9V X 0.274A
(d) 11V X 0.330A
(e) 13V X 0.390A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45
35
25
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time(sec)
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(e)
(d)
(c)
(b)
(a)
(a) 5V X 0.038A
(b) 7V X 0.054A
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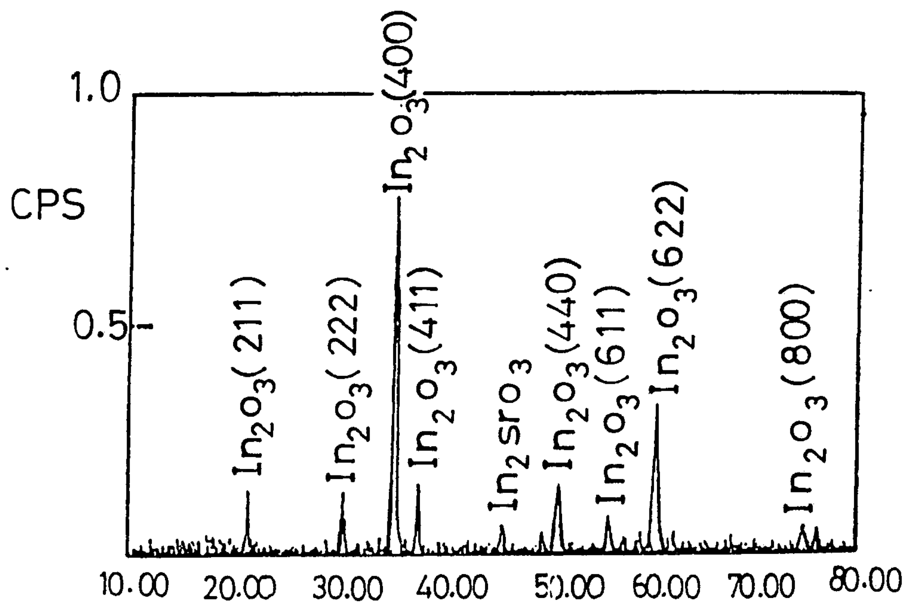
(d) 11V X 0.086A
(e) 13V X 0.104A
(f) 13.8V X 0.114A

FIG. 6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10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 92/00081

A. CLASSIFICATION OF SUBJECT MATTER

IPC^5: C 23 C 14/18, 14/08; C 03 C 17/06, 17/23

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

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Minimum documentation searched (classification system followed by classification symbols)

IPC^5: C 23 C, C 03 C

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 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.
A	DE, A1, 3 933 713 (MATSUSHITA ELECTRIC WORKS, LTD.) 12 April 1990 (12.04.90), claims 1-9.	1,4
A	EP, A2, 0 447 850 (NIHON SHINKU GIJUTSU KABUSHIKI KAISHA) 25 September 1991 (25.09.91), claims; column 1, lines 3-9.	2,5
A	EP, A1, 0 293 645 (SIEMENS AKTIENGESELLSCHAFT) 07 December 1988 (07.12.88), claims; column 3, lines 20-56.	2,3,5

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26 February 1993 (26.02.93)	03 March 1993 (03.03.93)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 92/00081

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DE A1 3933713	12-04-90	DE C2 3933713 US A 4964962 JP A2 2194163	14-11-91 23-10-90 31-07-90
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