United States Patent [19]

Ichinose et al.

[11] **3,926,858**

[45] **Dec. 16, 1975**

[54] **MOISTURE SENSITIVE ELEMENT**

[75] Inventors: **Noboru Ichinose**, Yokohama; **Yuhji Yokomizo; Masaki Katsura**, both of Tokyo, all of Japan

[73] Assignee: **Tokyo Shibaura Electric Co., Ltd.**, Kawasaki, Japan

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[21] Appl. No.: **487,533**

[30] **Foreign Application Priority Data**

July 13, 1973	Japan	48-78476
July 13, 1973	Japan	48-78477
Aug. 13, 1973	Japan	48-78478
Sept. 20, 1973	Japan	48-105455
Sept. 20, 1973	Japan	48-105456

[52] **U.S. Cl.** **252/517;** 252/518; 252/519; 252/520; 252/521

[51] **Int. Cl.**[2] **H01B 1/00**

[58] **Field of Search** 252/517–521; 338/20

[56] **References Cited**

UNITED STATES PATENTS

3,766,098 10/1973 Masuyama et al. 252/519

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—E. Suzanne Parr
Attorney, Agent, or Firm—Stewart and Kolasch, Ltd.

[57] **ABSTRACT**

A moisture sensitive element formed of an oxide complex semiconductor comprising 89.9 to 20 mol% of ZnO, 0.1 to 20 mol% of Cr_2O_3 and 10 to 60 mol% of at least one member selected from oxides of certain kinds of mono-, di-, tetra-, penta- and hexavalent metals.

8 Claims, 37 Drawing Figures

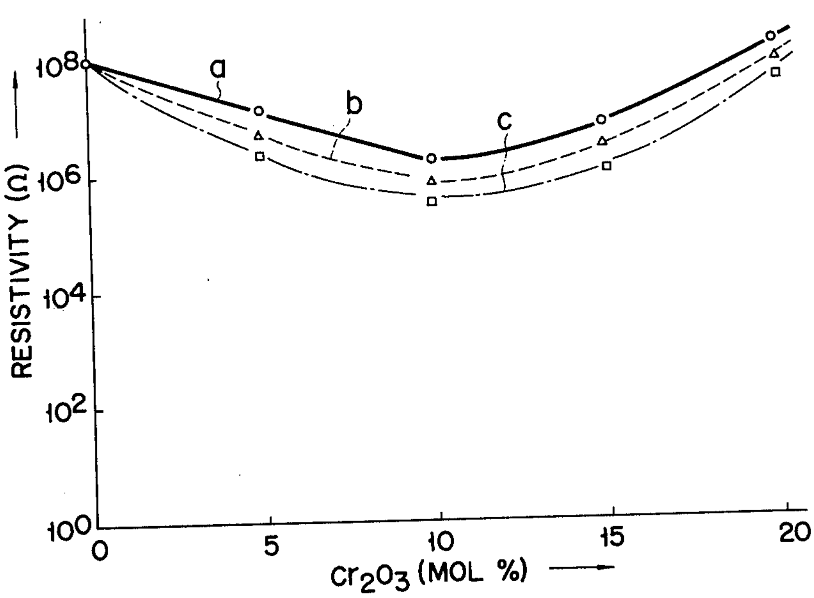


FIG. 1

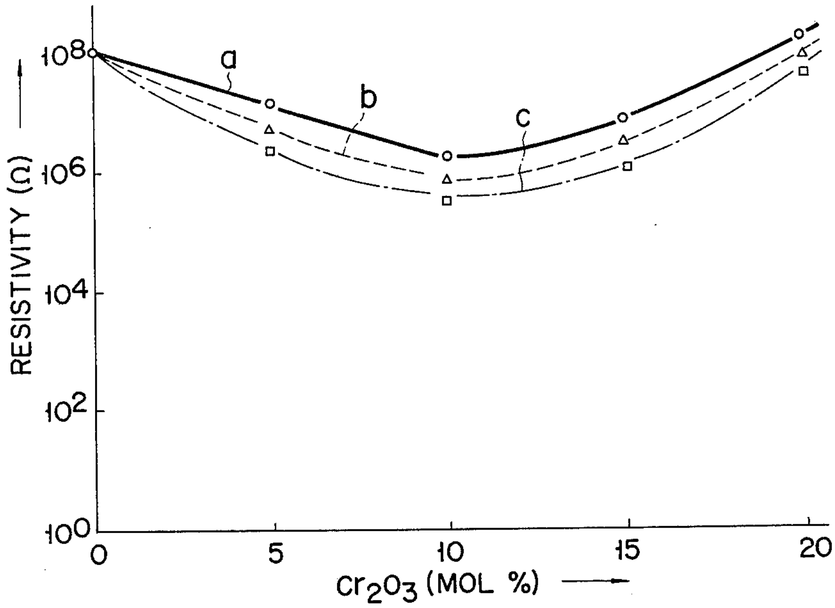

RESISTIVITY (Ω)
10^8
10^6
10^4
10^2
10^0
a
b
c
0
5
10
15
20
Cr_2O_3 (MOL %)

FIG. 2

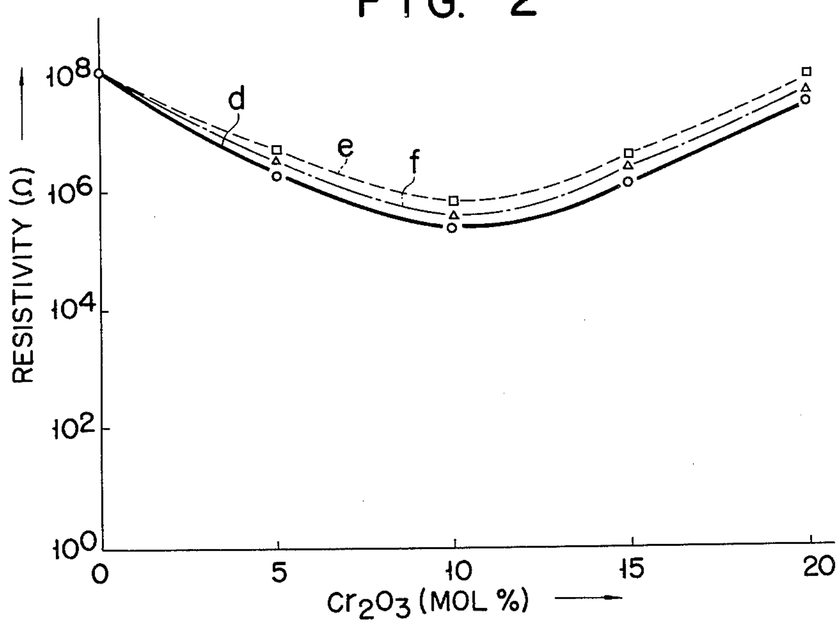

RESISTIVITY (Ω)
10^8
10^6
10^4
10^2
10^0
d
e
f
0
5
10
15
20
Cr_2O_3 (MOL %)

FIG. 3

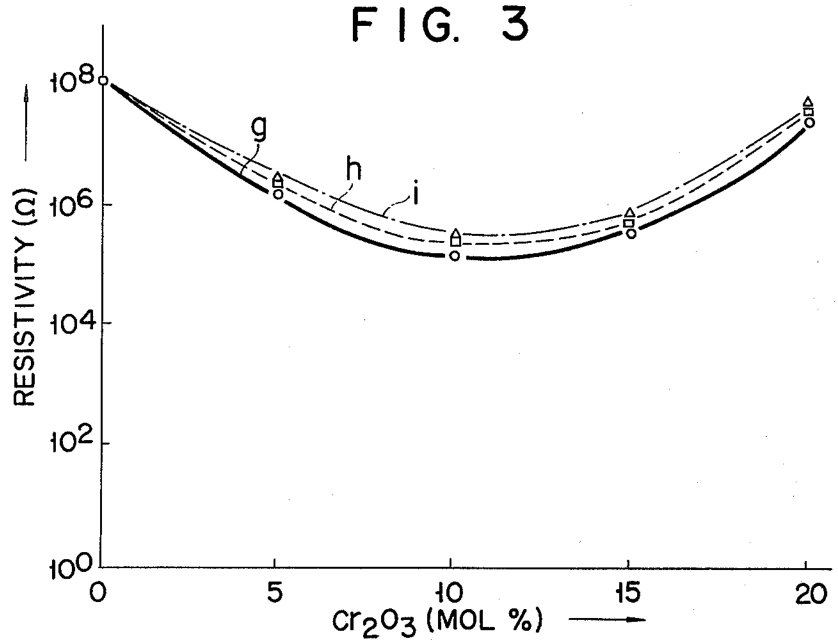

RESISTIVITY (Ω)
10^8
10^6
10^4
10^2
10^0
g
h
i
0
5
10
15
20
Cr_2O_3 (MOL %)

FIG. 4

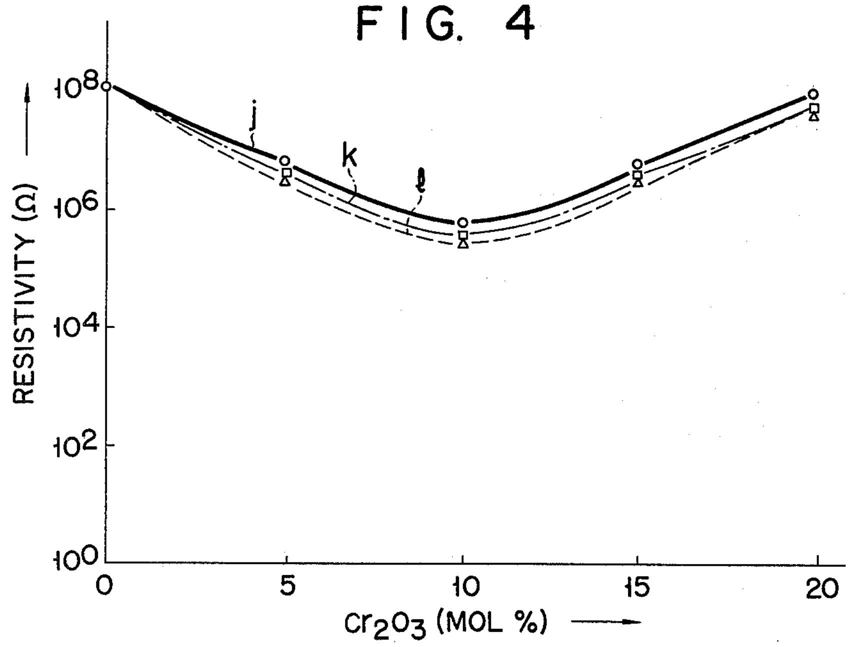
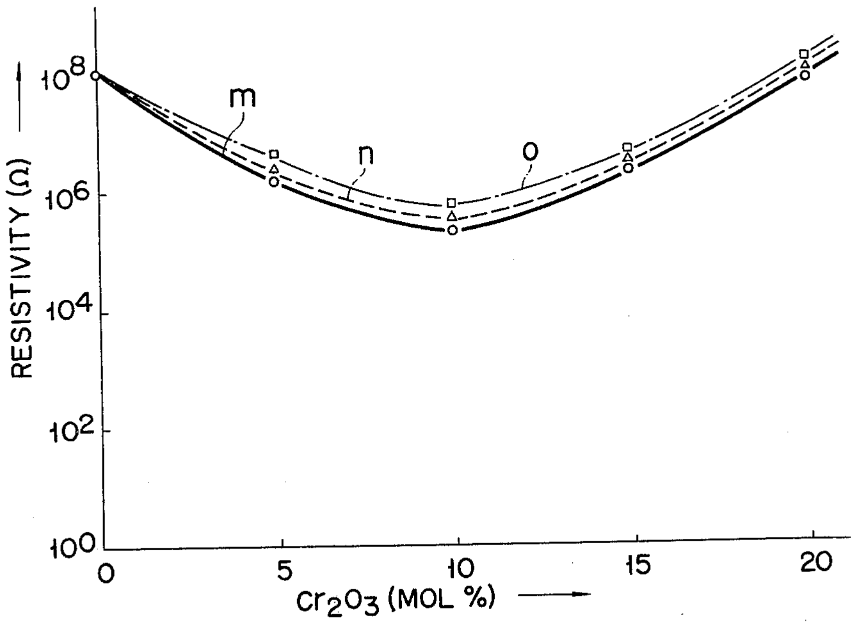

RESISTIVITY (Ω)
10^8
10^6
10^4
10^2
10^0
j
k
ℓ
0
5
10
15
20
Cr_2O_3 (MOL %)

FIG. 5



RESISTIVITY (Ω)
10^8
10^6
10^4
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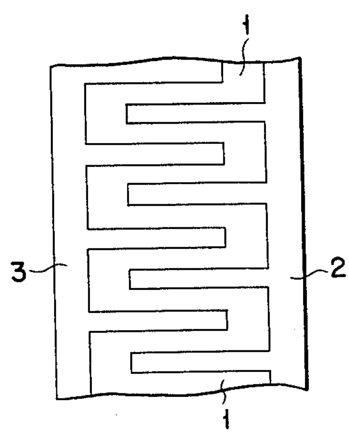
10^0
m
n
o
0
5
10
15
20
Cr_2O_3 (MOL %)

FIG. 6



1
2
3
1

FIG. 7

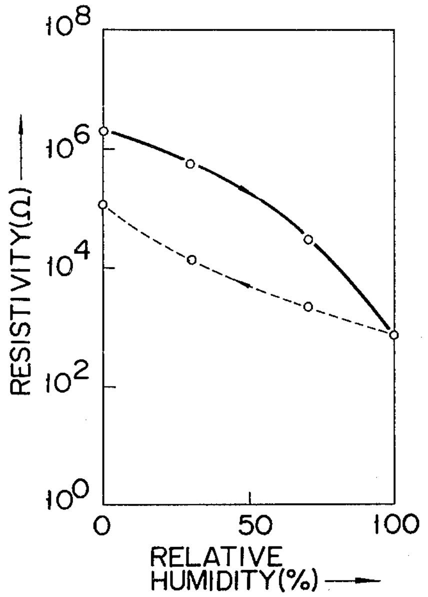


FIG. 8

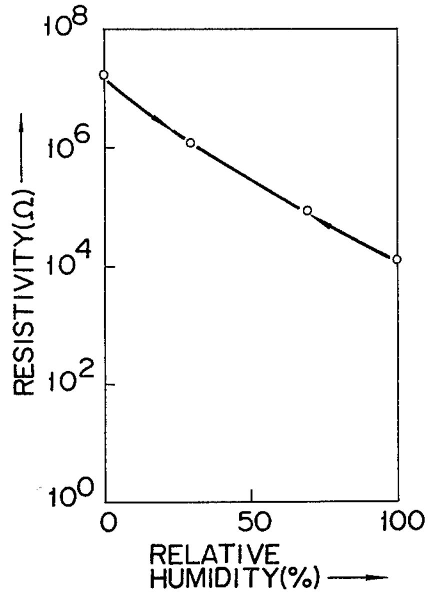


FIG. 9

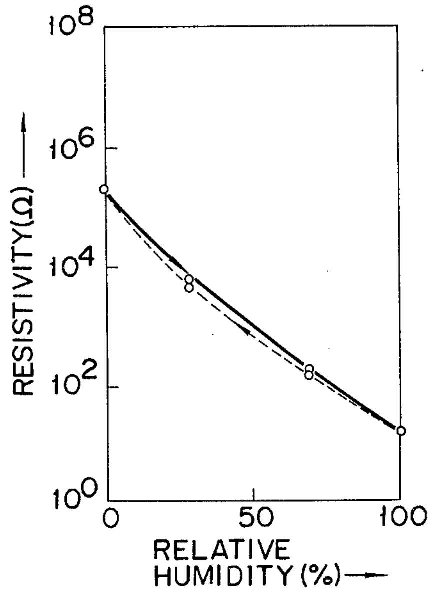


FIG. 10

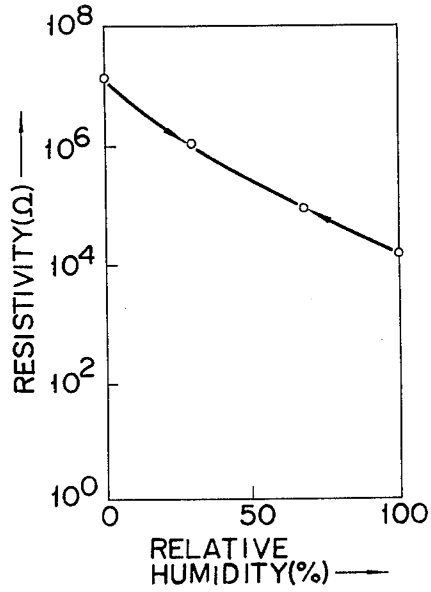


FIG. 11

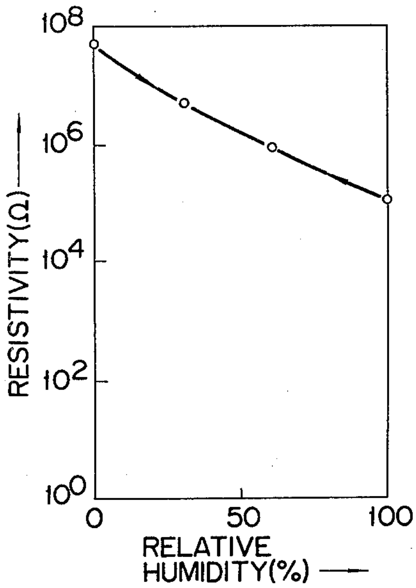


FIG. 12

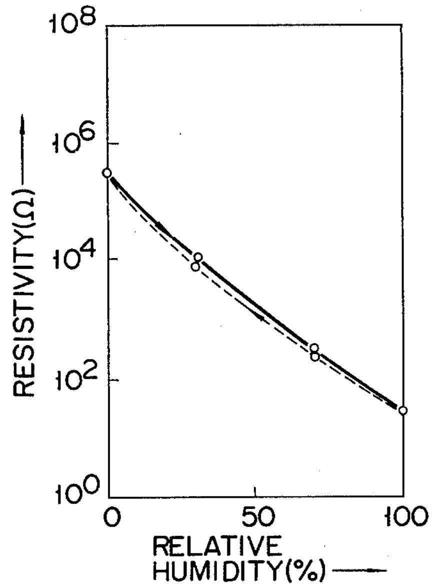


FIG. 13

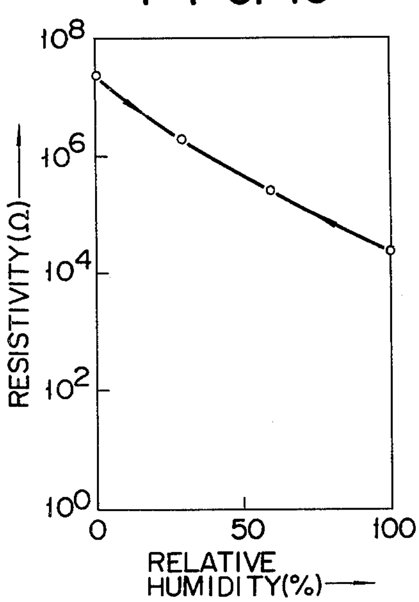


FIG. 14

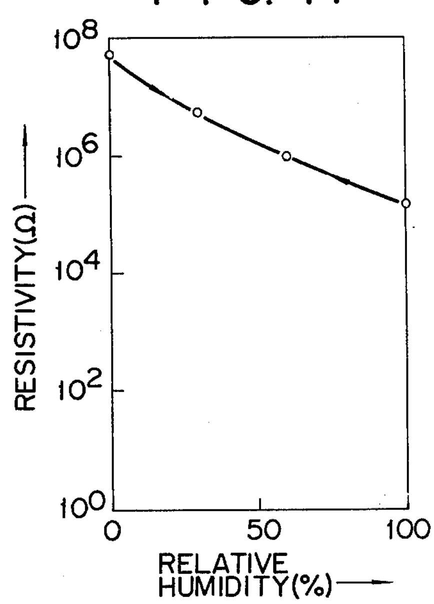


FIG. 15

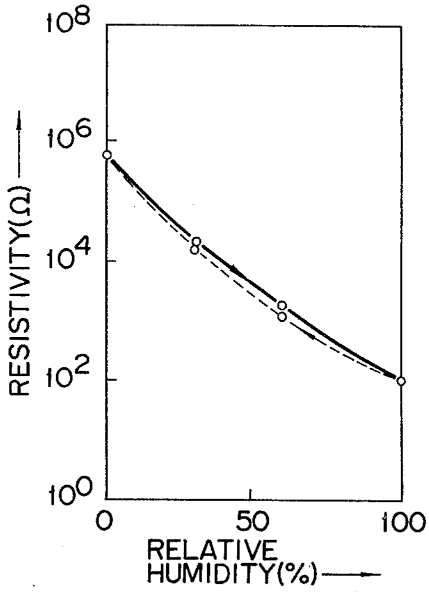


FIG. 16

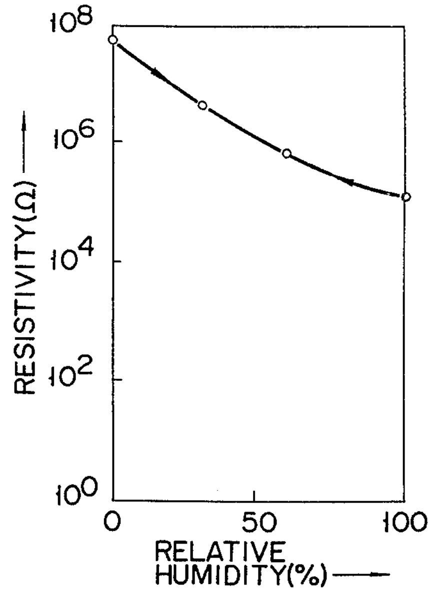


FIG. 17

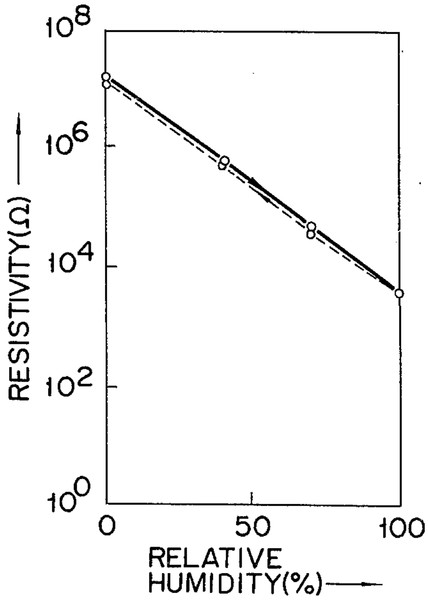


FIG. 18

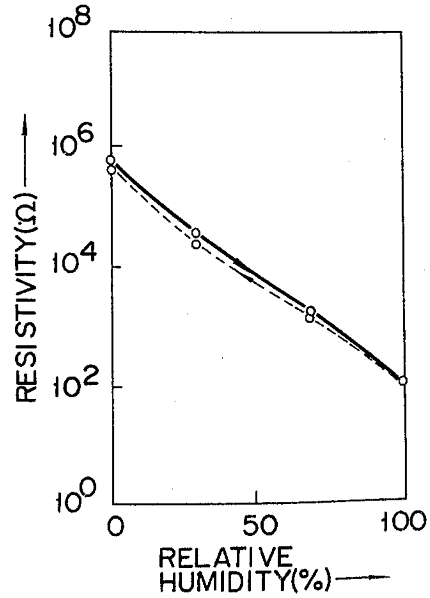


FIG. 19

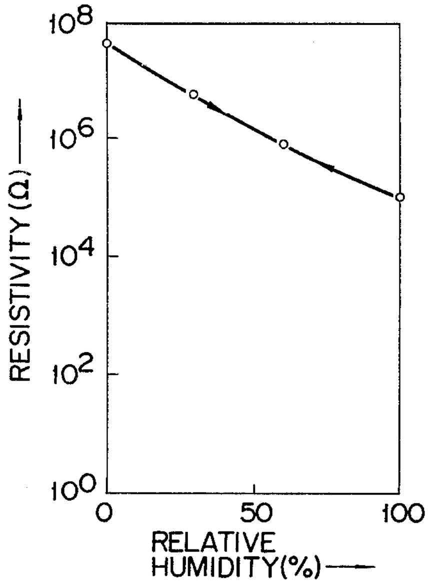


FIG. 20

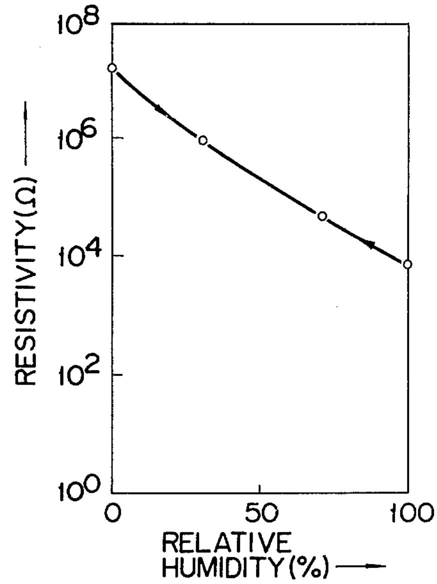


FIG. 21

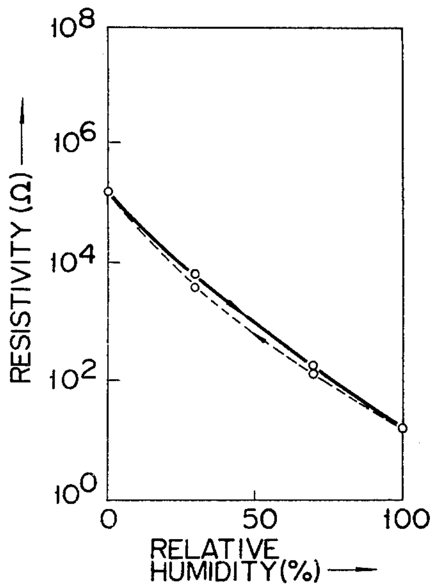


FIG. 22

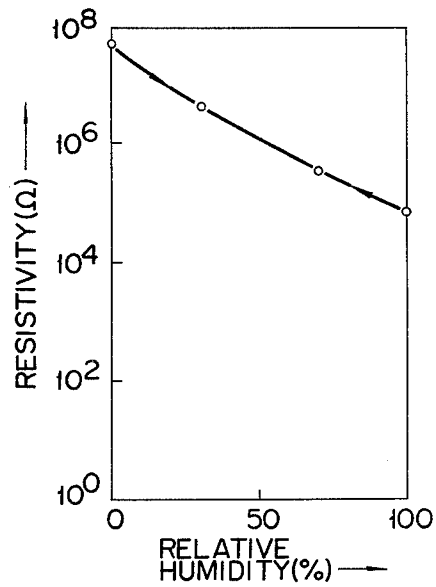


FIG. 23

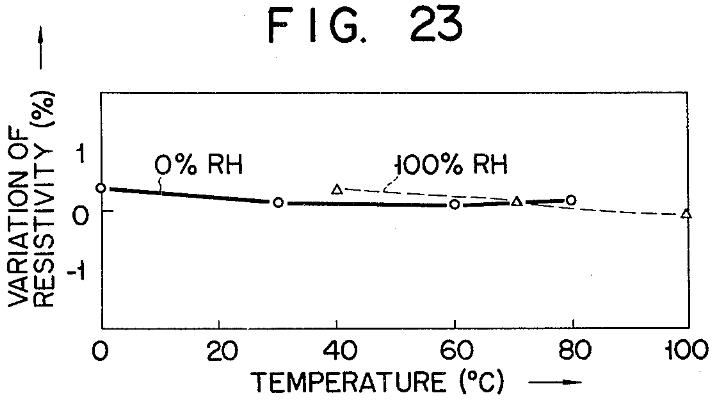


FIG. 24

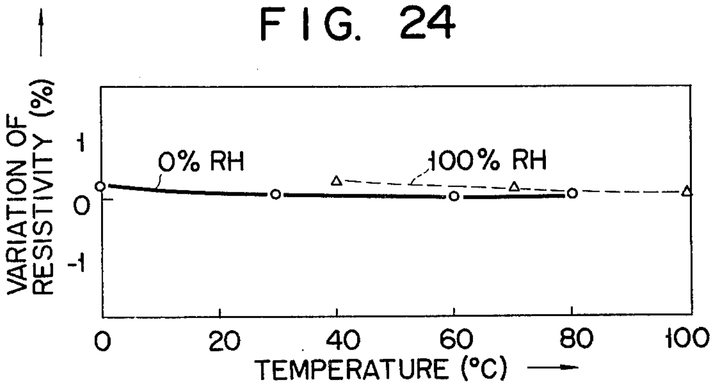


FIG. 25

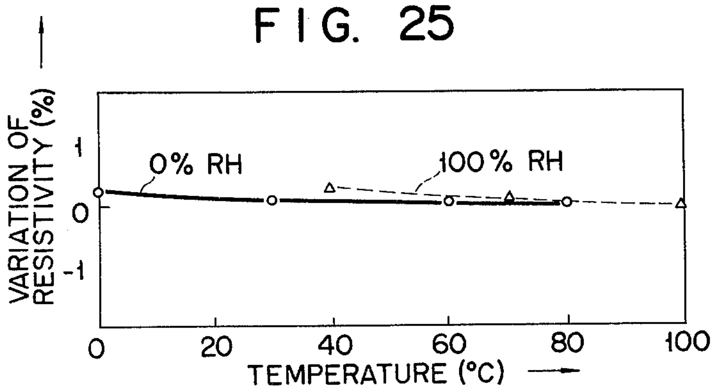


FIG. 26

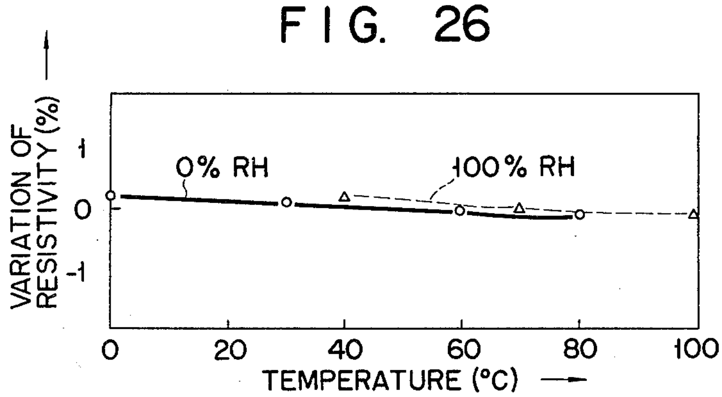


FIG. 27

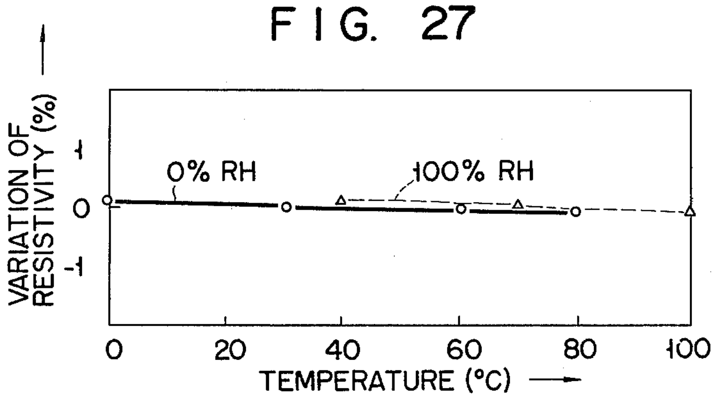


FIG. 28

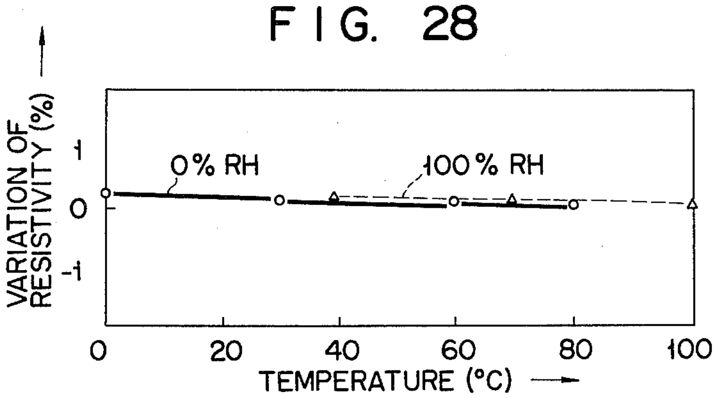


FIG. 29

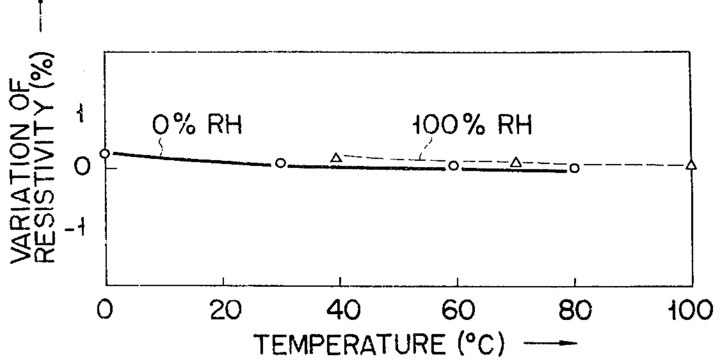


FIG. 30

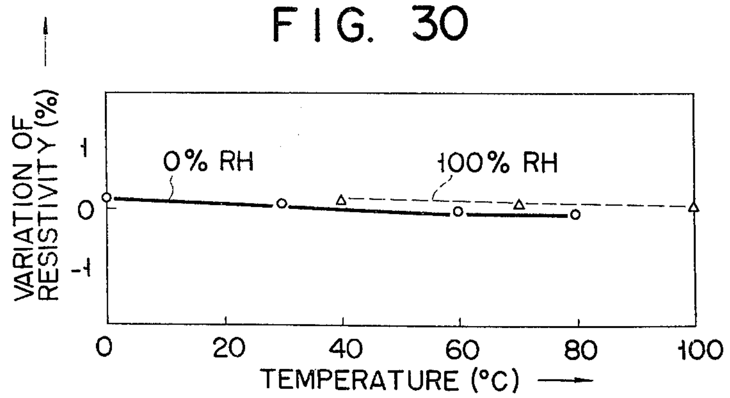


FIG. 31

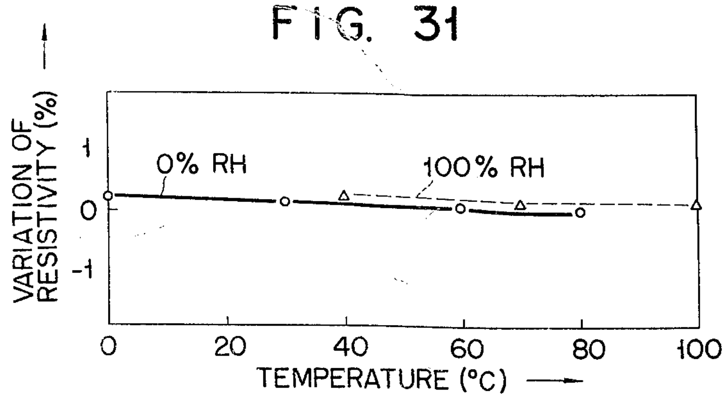


FIG. 32

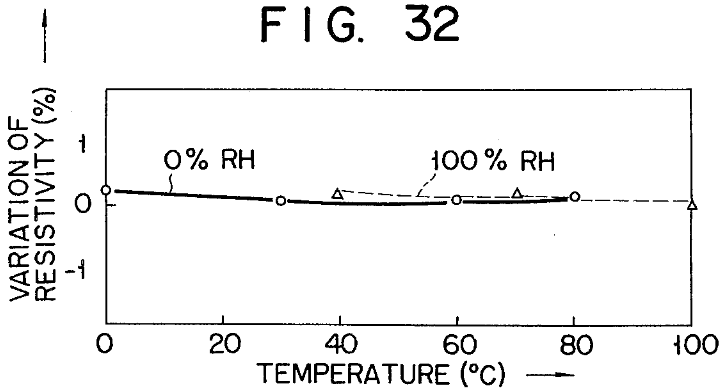


FIG. 33

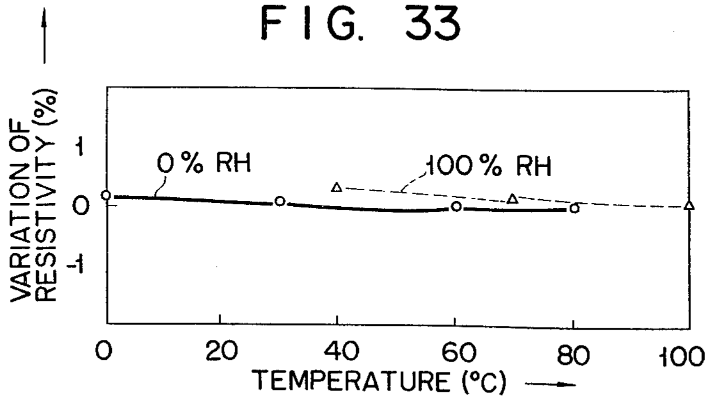
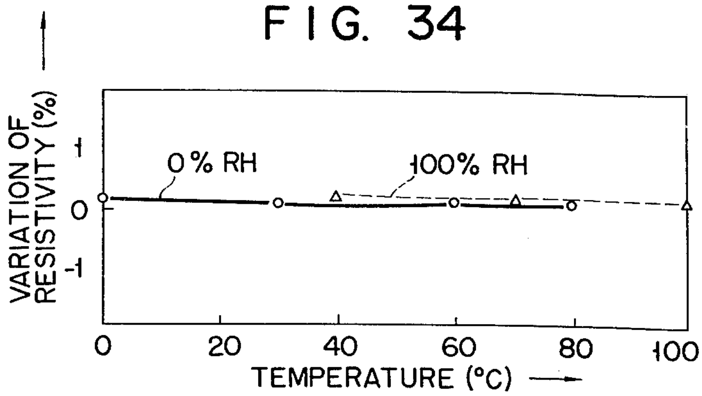
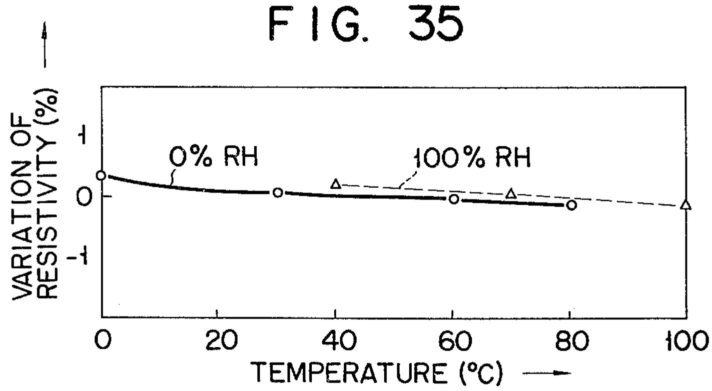


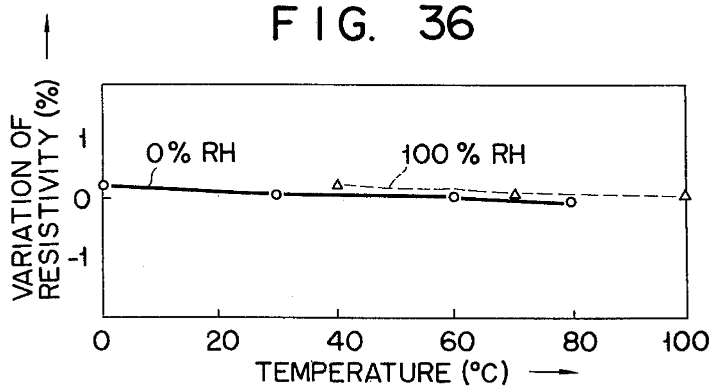
FIG. 34



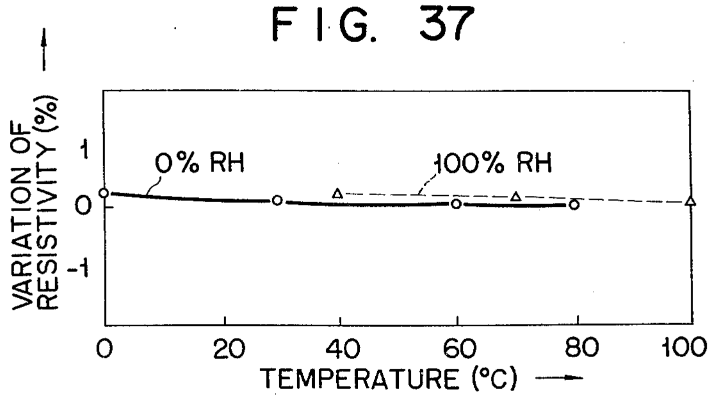
F I G. 35



F I G. 36



F I G. 37



MOISTURE SENSITIVE ELEMENT

This invention relates to a moisture sensitive element which detects the variation of humidity with electric resistivity, and more particularly to an element formed of an oxide complex semiconductor.

A prior art moisture sensitive element comprises a fine powder of a metal oxide such as Fe_3O_4, Fe_2O_3, Al_2O_3 and Cr_2O_3 which is coated on an inorganic insulating substrate. This sensitive element is based on excellent hygroscopicity which the metal oxide generally has. The coated powder of the metal oxide exhibits significant variation in electric resistivity in response to the variation in ambient humidity. Further, a moisture sensitive element utilizing metal oxide film is known. This element has small weight and size, and promptly responds to humidity changes. In addition it satisfactorily functions over a wide range of temperatures, from a low to a high temperature.

However, although the element using powdery metal oxide is physically, chemically, and thermally stable, the coated layer of powdery metal oxide generally has high resistivity and therefore the element hardly detects electrically the changes of humidity with accuracy when such changes are small. Moreover, its reproducibility of the measured value and aging property are not satisfactory. The element based on metal oxide film sometimes fails to measure the humidity accurately, and is inferior in sensitivity due to the unstability and nonhomogeneity of the film. In addition the element can hardly be mass produced.

A group of materials called oxide semiconductors which are prepared essentially from metal oxides may be used in a moisture sensitive element since the oxide semiconductor has lower resistivity than raw metal oxide and is therefore assumed to show great changes in resistivity due to the absorption and release of moisture. However, most of the oxide semiconductors have, as they are called thermistors (i.e., thermally sensitive resistors), a great negative temperature coefficient of resistivity and their resistivities are much affected by only a little change of temperature. The utilization of the oxide semiconductor has therefore been neglected in measurement of humidity accompanied with variation of temperature.

It is an object of the invention to provide a moisture sensitive element suffering little from aging and having a high sensitivity, a high reproducibility of the measured value, and a small temperature coefficient of resistivity.

Another object of the invention is to provide a moisture sensitive element formed of an oxide complex semiconductor.

In accordance with this invention there is provided a moisture sensitive element formed of an oxide complex semiconductor comprising 89.9 to 20 mol% of ZnO, 0.1 to 20 mol% of Cr_2O_3 and 10 to 60 mol% of at least one of the third metal oxides selected from the group consisting of Li_2O, Na_2O, K_2O, Rb_2O, Cu_2O, BaO, SrO, CaO, PbO, MnO, NiO, CoO, MgO, CdO, CuO, FeO, BeO, TiO_2, GeO_2, ZrO_2, MnO_2, TeO_2, SnO_2, SiO_2, CeO_2, ThO_2, HfO_2, Nb_2O_5, Ta_2O_5, Sb_2O_5, V_2O_5, WO_3, MoO_3, and TeO_3.

This invention can be more fully understood from the following detailed description when taken in connection with reference to the accompanying drawings, in which:

FIG. 1 shows the content of Cr_2O_3 and the resistivity of ZnO-$Me_2^{(1)}O$—Cr_2O_3 system in which the molar ratio of $Me_2^{(1)}O$ to ZnO is rendered constant;

FIG. 2 shows the content of Cr_2O_3 and the resistivity of ZnO-$Me^{(2)}O$-Cr_2O_3 system in which the molar ratio of $Me^{(2)}O$ to ZnO is rendered constant;

FIG. 3 shows the content of Cr_2O_3 and the resistivity of ZnO-$Me^{(3)}O_2$-Cr_2O_3 system in which the molar ratio of $Me^{(3)}O_2$ to ZnO is rendered constant;

FIG. 4 shows the content of Cr_2O_3 and the resistivity of ZnO-$Me_2^{(4)}O_5$-Cr_2O_3 system in which the molar ratio of $Me_2^{(4)}O_5$ to ZnO is rendered constant;

FIG. 5 shows the content of Cr_2O_3 and the resistivity of ZnO-$Me^{(5)}O_3$-Cr_2O_3 system in which the molar ratio of $Me^{(5)}O_3$ to ZnO is rendered constant;

FIG. 6 shows a plan view of a humidity measuring device using a moisture sensitive element according to this invention;

FIG. 7 shows the relationship between the humidity and the resistivity of a prior art moisture sensitive element at a constant temperature;

FIGS. 8 to 22 show the relationship between the humidity and the resistivity of the moisture sensitive elements according to this invention at a constant temperature; and

FIGS. 23 to 37 show the relationship between the temperature and the resistivity of the moisture sensitive elements according to this invention at a constant humidity.

This invention is based on the discovery that even an oxide semiconductor, though classified as a thermistor, turns out a moisture sensitive element having a low resistivity and a small temperature coefficient of resistivity if its composition ratio is defined as above. Such an element exhibits a resistivity greatly changing with the humidity variation and being little affected by ambient temperature.

The oxide semiconductor forming a moisture sensitive element of the invention contains, in addition to ZnO and Cr_2O_3, at least one oxide of certain mono-, di-, tetra-, penta- and hexavalent metals (the oxide being hereinafter referred to as the third metal oxide). The oxide ($Me_2^{(1)}O$) of monovalent metals of the third metal oxide is selected from Li_2O, Na_2O, K_2O, Rb_2O and Cu_2O, that ($Me^{(2)}O$) of divalent metals from BaO, SrO, CaO, PbO, MnO, NiO, CoO, MgO, CdO, CuO, FeO and BeO, that ($Me^{(3)}O_2$) of tetravalent metals from TiO_2, GeO_2, ZrO_2, MnO_2, TeO_2, SnO_2, SiO_2, CeO_2, ThO_2 and HfO_2, that ($Me_2^{(4)}O_5$) of pentavalent metals from Nb_2O_5, Ta_2O_5, Sb_2O_5 and V_2O_5. and that ($Me^{(5)}O_3$) of hexavalent metals from WO_3, MoO_3 and TeO_3. Any mixture of the third metal oxide may be used in the invention.

The content of ZnO is 89.9 to 20 mol%, preferably 80 to 30 mol%, that of Cr_2O_3 0.1 to 20 mol%, preferably 5 to 20 mol%, and that of the third metal oxide 10 to 60 mol%, preferably 15 to 50 mol%. When the content of Cr_2O_3 is less than 0.1 mol% and/or when that of the third metal oxide is less than 10 mol%, the resultant element has a resistivity as large as 100 MΩ, and is a poor moisture sensitive element. This is true also when the content of ZnO is less than 20 mol% and/or when that of the third metal oxide exceeds 60 mol%.

When the content (mol%) of Cr_2O_3 is varied with the molar ratio of the third metal oxide to ZnO fixed at 1:3, the resultant oxide complex semiconductors have the resistivity characteristics as shown in FIGS. 1 to 5. FIG. 1 indicates the resistivity characteristics of the semiconductor containing the third metal oxide $Me_2^{(1)}O$, in which curves *a*, *b* and *c* represent the resistivity characteristics in the case where $Me^{(1)}$ are Li, K and Cu, respectively. FIG. **2** indicates the resistivity characteristics of the semiconductor containing the third metal oxide $Me^{(2)}O$, in which curves *d*, *e* and *f* represent the resistivity characteristics in the case where $Me^{(2)}$ are Sr, Ni and Co, respectively. FIG. **3** shows the resistivity characteristics of the semiconductor containing the third metal oxide $Me^{(3)}O_2$, in which curves *g*, *h* and *i* represent the resistivity characteristics in the case where $Me^{(3)}$ are Ti, Sn and Ce, respectively. FIG. **4** shows the resistivity characteristics of the semiconductor containing the third metal oxide $Me_2^{(4)}O_5$, in which curves *j*, *k* and *l* represent the resistivity characteristics in the case where $Me^{(4)}$ are Ta, Sb and V, respectively. FIG. **5** indicates the resistivity characteristics of the semiconductor containing the third metal oxide $Me^{(5)}O_3$, in which curves *m*, *n* and *o* represent the resistivity characteristics in the case where $Me^{(5)}$ are W, Mo and Te, respectively.

As these figures indicate, a content of Cr_2O_3 more than 20 mol% causes the resultant semiconductor to have a resistivity of over 100 MΩ and to become an unsuitable moisture sensitive element. All the above being considered, it is apparent that the upper limit of ZnO content is 89.9 mol%. Particularly, a mixture of 60 mol% of ZnO, 10 mol% of Cr_2O_3 and 30 mol% of the third metal oxide can make a highly desirable moisture sensitive element.

The moisture sensitive element of this invention may be prepared in the following manner. Raw metal oxides accurately weighed out in prescribed amounts are mixed together in a ball mill and presintered at a relatively low temperature, for example, at 600° to 900°C. The presintered mass is pulverized into powder. The raw materials used may be metal compounds such as a hydroxide, carbonate and oxalate which can be converted to the oxide upon heating.

The powder thus obtained is mixed with a binder such as polyvinyl alcohol, and the mixture is shaped, under a pressure of about 100 to 1,000 kg/cm², into, for example, a plate having a width of 10 mm, a length of 20 mm and a thickness of 1 mm. The plate is sintered at about 1,000° to 1,300°C generally in air. During sintering, it is kept at a maximum temperature for 1 to 5 hours.

The moisture sensitive element prepared as above is constructed in, for example, a humidity measuring device as shown in FIG. **6**. In the figure, numeral **1** denotes the moisture sensitive element of the invention, and numerals **2** and **3** electrodes made of material such as a high-temperature baking silver paint which well adheres to and has a little contact resistance with the element **1**.

The moisture sensitive element of the invention, though unexpectedly composed of the oxide semiconductor, has its resistivity hardly changed with temperature. Further, it exhibits such an excellent aging property that its resistivity varied within only several percents even it has been used for a long period of time. Its resistivity variation accompanying with its aging is negligibly small as mentioned above. The element is therefore practically satisfactory. Furthermore, it responds to humidity variation far more quickly than a prior art element. Its sensitivity or responding speed is such that it responds in about 10 seconds to 0-to-100 percent humidity change, and in 2 seconds after a humidity change of ±20 percent. A prior art element responds in about 40 seconds and in 5 to 7 seconds to 0-to-100 percent and ±20 percent humidity changes, respectively. With respect to the element of the invention no or little difference occurs between the plotted value of resistivity measured by a decreasing humidity and that measured conversely by increasing humidity. In addition the element of the invention can be manufactured economically since the raw materials used are obtained cheeply.

It has not yet been fully understood why the moisture sensitive element of the invention shows such an excellent characteristic as described above. However, it is assumed that when water vapor deposits on a surface of the element, the element becomes electrically conductive just as a semiconductor becomes, as is well known, when it adsorbs a gas.

This invention will be more clearly understood with reference to the following Examples.

EXAMPLES

Mixtures of 90 to 18 mol% of ZnO, 0 to 22 mol% of Cr_2O_3 and 10 to 62 mol% of the third metal oxide were weighed out as will be indicated below in the Tables and well mixed in a ball mill. The mixture was presintered at 800°C for 1 hour and pulverized into a powder, to which was added polyvinyl alcohol as a binder. The mixture obtained was shaped into a plate 10 mm wide, 20 mm long and 1 mm thick. The plate was sintered for 2 hours at 1,000 kg/cm² in an electric furnace kept at 1,100° to 1,300°C. Thus, 174 kinds of plate samples including controls were prepared.

To the plate was ordinarily baked silver electrodes, forming a humidity measuring device. Either an elemental Ag or Ag_2O may be used as a starting material for the silver electrodes. Since the sintered mass is stable to temperature, the electrode could be baked over a wide temperature range of, for example, 400° to 800°C.

With respect to each sample the resistivity (R_{25}(0% RH)) which was measured at 25°C and a relative humidity of 0 percent, and the ratio (R_{25}(0% RH)/R_{25}(100% RH)) of the resistivity at 25°C and a relative humidity of 0 percent to that at 25°C and a relative humidity of 100 percent were obtained as shown in Tables 1 to 6. Table 1 shows the results with respect to samples containing the third metal oxide $Me_2^{(1)}O$, Table 2 the results with respect to samples containing the third metal oxide $Me^{(2)}O$, Table 3 the results with respect to samples containing the third metal oxide $Me^{(3)}O_2$, Table 4 the results with respect to samples containing the third metal oxide $Me_2^{(4)}O_5$, Table 5 the results with respect to samples containing the third metal oxide $Me^{(5)}O_3$, and Table 6 the results with respect to samples containing a mixture of the third metal oxides $Me_2^{(1)}O$, $Me^{(2)}O$, $Me^{(3)}O_2$, $Me_2^{(4)}O_5$ and $Me^{(5)}O_3$.

Some of the above-mentioned samples were tested for resistivity characteristics to humidity variation with the temperature kept at 25°C. The results are indicated in FIGS. **8** to **22**, which show the characteristics of the samples of Examples 6, 13, 23, 57, 60, 78, 90, 100, 113, 117, 126, 135, 139 and 146, respectively.

As a comparison, the resistivity-humidity characteristics of a prior art element formed of a sintered mixture of silicon and a metal oxide are indicated in FIG. **7**. This figure reveals that appreciable difference occurs between resistivity measured by a decreasing humidity and that measured conversely by increasing humidity. On the contrary, the moisture sensitive element of the invention gives rise to, as is apparent from FIGS. **8** to **22**, no or only a little of such a difference, indicating that it reproduces the measured value much more highly than the prior art element.

Moreover, the resistivity characteristics to temperature variations at relative humidities of 0 and 100 percent were measured with respect to some of the samples. The samples show such characteristics as illustrated in FIGS. **23** to **37**. FIGS. **23** to **37** show the resistivity characteristics of the samples of Examples 3, 15, 25, 39, 50, 66, 74, 91, 102, 111, 116, 126, 132, 137 and 147, respectively. These figures clearly show that the moisture sensitive element of the invention, though comprised of the oxide semiconductor, indicates a resistivity which changes little with temperature variation.

Table 1

		ZnO (mol%)	Cr_2O_3 (mol%)	$Me_2^{(1)}O$ (mol%)			R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Control	1	90	0	$Me^{(1)}$	=Li	10	155	175
''	2	''	''	''	=Na	''	170	190
Example	1	89.9	0.1	''	=Li	''	74	785
''	2	''	''	''	=Na	''	63	810
''	3	''	''	''	=K	''	57	745
''	4	''	''	''	=Rb	''	61	830
''	5	''	''	''	=Cu	''	78	710
''	6	80	5.0	''	=Li	15	20	1640
''	7	''	''	''	=Na	''	13	1855
''	8	''	''	''	=K	''	17	1705
''	9	''	''	''	=Rb	''	11	2080
''	10	''	''	''	=Cu	''	24	1570
Example	11	80	5.0	{ $Me^{(1)}$	=Na	3	10	2120
				''	=K	''		
				''	=Rb	''		
				''	=Cu	''		
				''	=Li	''		
''	12	60	10	''	=Li	30	0.50	8090
''	13	''	''	''	=Na	''	0.26	10770
''	14	''	''	''	=K	''	0.34	9565
''	15	''	''	''	=Rb	''	0.47	9135
''	16	''	''	''	=Cu	''	0.63	7940
''	17	''	''	{ ''	=Li	10	0.38	9675
				''	=Na	''		
				''	=K	''		
''	18	''	''	{ ''	=K	''	0.42	9310
				''	=Rb	''		
				''	=Cu	''		
''	19	30	20	''	=Li	50	28	1605
''	20	''	''	''	=Na	''	34	1410
''	21	''	''	''	=K	''	40	1300
''	22	''	''	''	=Rb	''	46	1175
''	23	''	''	''	=Cu	''	22	1685
''	24	''	''	{ ''	=Li	10	20	1720
				''	=Na	''		
				''	=K	''		
				''	=Rb	''		
				''	=Cu	''		
''	25	20	''	''	=Li	60	70	845
''	26	''	''	''	=Na	''	78	810
Example	27	20	20	$Me^{(1)}$	=K	60	83	760
''	28	''	''	''	=Rb	''	87	720
''	29	''	''	''	=Cu	''	65	905
''	30	''	''	{ ''	=Li	30	69	885
				''	=K	''		
''	31	''	''	{ ''	=Rb	''	62	920
				''	=Cu	''		
Control	3	18	20	''	=K	62	156	180
''	4	''	22	''	=Cu	60	215	145

Table 2

		ZnO (mol%)	Cr_2O_3 (mol%)	$Me^{(2)}O$ (mol%)			R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Control	5	90	0	$Me^{(2)}$	=Ba	10	200	185
''	6	''	''	''	=Ca	''	150	190
Example	32	89.9	0.1	''	=Ba	''	75	545
''	33	''	''	''	=Sr	''	82	590
''	34	''	''	''	=Ca	''	66	640
''	35	''	''	''	=Pb	''	87	735
''	36	''	''	''	=Mn	''	73	560
''	37	''	''	''	=Ni	''	61	705
''	38	''	''	''	=Co	''	58	680
''	39	''	''	''	=Mg	''	60	770
''	40	''	''	''	=Cd	''	69	710
''	41	''	''	''	=Cu	''	74	665
''	42	''	''	''	=Fe	''	77	635
''	43	''	''	''	=Be	''	85	520
''	44	80	5.0	''	=Ba	15.0	31	1435
Example	45	80	5.0	$Me^{(2)}$	=Ca	15.0	28	1620
''	46	''	''	''	=Pb	''	12	1915

Table 2-continued

		ZnO (mol%)	Cr_2O_3 (mol%)		$Me^{(2)}O$ (mol%)		R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
"	47	"	"	"	=Ni	"	22	1535
"	48	"	"	"	=Co	"	17	1820
"	49	"	"	"	=Mg	"	26	1580
"	50	"	"	"	=Fe	"	35	1325
"	51	"	"	"	=Sr	3	14	1870
				"	=Mn	"		
				"	=Co	"		
				"	=Ni	"		
				"	=Be	"		
"	52	60	10	"	=Ca	30	0.65	6730
"	53	"	"	"	=Pb	"	0.51	9315
"	54	"	"	"	=Cd	"	0.74	6040
"	55	"	"	"	=Cu	"	0.86	7225
"	56	"	"	"	=Co	"	0.97	5655
"	57	"	"	"	=Ba	10	0.48	9635
				"	=Sr	"		
				"	=Ca	"		
"	58	"	"	"	=Pb	"	0.58	8710
				"	=Cu	"		
				"	=Co	"		
"	59	30	20	"	=Ca	50	37	1075
"	60	"	"	"	=Co	"	40	1020
"	61	"	"	"	=Fe	"	28	1320
"	62	"	"	"	=Cu	"	32	1145
"	63	"	"	"	=Ba	5	23	1400
				"	=Sr	"		
				"	=Ca	"		
				$Me^{(2)}$	=Pb	5		
				"	=Mn	"		
				"	=Ni	"		
				"	=Co	"		
				"	=Fe	"		
				"	=Cu	"		
				"	=Cd	"		
Example	64	20	20	"	=Sr	60	75	735
"	65	"	"	"	=Fe	"	83	655
"	66	"	"	"	=Ni	"	90	560
"	67	"	"	"	=Be	"	71	770
"	68	"	"	"	=Ba	"	67	805
"	69	"	"	"	=Ca	10	70	795
				"	=Pb	"		
				"	=Mn	"		
				"	=Ni	"		
				"	=Co	"		
				"	=Fe	"		
Control	7	18	20	"	=Cd	62	170	160
"	8	"	22	"	=Mg	60	240	125

Table 3

		ZnO (mol%)	Cr_2O_3 (mol%)		$Me^{(3)}O_2$ (mol%)		R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Control	9	90	0	$Me^{(3)}$	=Ti	10	180	180
"	10	"	"	"	=Ge	"	145	195
Example	70	89.9	0.1	"	=Ti	"	72	610
"	71	"	"	"	=Ge	"	86	575
"	72	"	"	"	=Zr	"	61	790
"	73	"	"	"	=Mn	"	74	605
"	74	"	"	"	=Te	"	69	590
"	75	"	"	"	=Sn	"	57	860
"	76	"	"	"	–Si	"	60	825
"	77	"	"	"	=Ce	"	65	780
"	78	"	"	"	=Th	"	73	595
"	79	"	"	"	=Hf	"	79	535
"	80	80	5.0	"	=Ge	15.0	28	1630
"	81	"	"	"	=Zr	"	33	1445
"	82	"	"	"	=Mn	"	12	2070
"	83	"	"	"	=Te	"	19	1910
"	84	"	"	"	=Si	"	21	1765
"	85	"	"	"	=Ce	"	37	1320
"	86	"	"	"	=Ti	3.0	16	1880
				"	=Ge	"		
				"	=Zr	"		
				"	=Mn	"		
				"	=Te	"		
"	87	60	10	"	=Zr	30	0.39	10410
Example	88	60	10	$Me^{(3)}$	=Ge	30	0.45	8955
"	89	"	"	"	=Te	"	0.52	8060
"	90	"	"	"	=Mn	"	0.66	7120
"	91	"	"	"	=Ce	"	0.74	6535
"	92	"	"	"	=Ti	10	0.61	7685
"				"	=Ge	"		
				"	=Zr	"		
"	93	"	"	"	=Ce	"	0.77	6390
				"	=Hf	"		
				"	=Th	"		

Table 3-continued

		ZnO (mol%)	Cr_2O_3 (mol%)		$Me^{(3)}O_2$ (mol%)		R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
"	94	30	20	"	=Mn	50	26	1610
"	95	"	"	"	=Te	"	33	1325
"	96	"	"	"	=Sn	"	39	1285
"	97	"	"	"	=Si	"	44	1170
"	98	"	"	"	=Ti	5	21	1740
				"	=Ge	"		
				"	=Zr	"		
				"	=Mn	"		
				"	=Te	"		
				"	=Sn	"		
				"	=Si	"		
				"	=Ce	"		
				"	=Th	"		
				"	=Hf	"		
"	99	20	"	"	=Ti	60	71	765
"	100	"	"	"	=Zr	"	84	710
"	101	"	"	"	=Te	"	87	670
"	102	"	"	"	=Sn	"	69	785
"	103	"	"	"	=Si	"	60	820
Example	104	20	20	$Me^{(3)}$	=Hf	60	55	940
"	105	"	"	"	=Ge	10	62	805
				"	=Zr	"		
				"	=Mn	"		
				"	=Te	"		
				"	=Ce	"		
				"	=Sn	"		
Control	11	18	20	"	=Si	62	165	185
"	12	"	22	"	=Sn	60	220	130

Table 4

		ZnO (mol%)	Cr_2O_3 (mol%)		$Me_2^{(4)}O_5$ (mol%)		R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Control	13	90	0	$Me^{(4)}$	=Nb	10	200	175
"	14	"	"	"	=Ta	"	165	185
Example	106	89.9	0.1	"	=Nb	"	84	580
"	107	"	"	"	=Ta	"	76	635
"	108	"	"	"	=Sb	"	69	720
"	109	"	"	"	=V	"	77	615
"	110	80	5.0	"	=Nb	15.0	24	1720
"	111	"	"	"	=Ta	"	31	1560
"	112	"	"	"	=Sb	"	15	1895
"	113	"	"	"	=V	"	12	2035
"	114	"	"	"	=Nb	6.0	17	1770
				"	=Ta	3.0		
				"	=Sb	"		
				"	=V	"		
Example	115	60	10	$Me^{(4)}$	=Nb	30	0.55	8340
"	116	"	"	"	=Ta	"	0.68	8125
"	117	"	"	"	=Sb	"	0.76	7490
"	118	"	"	"	=V	"	0.91	6660
"	119	"	"	"	=Nb	15	0.72	7715
				"	=Sb	"		
				"	=Ta	"		
"	120	"	"	"	=V	"	0.69	8040
"	121	30	20	"	=Nb	50	24	1680
"	122	"	"	"	=Ta	"	36	1520
"	123	"	"	"	=Sb	"	19	1830
"	124	"	"	"	=V	"	38	1465
"	125	20	"	"	=Nb	60	67	775
"	126	"	"	"	=Ta	"	72	720
"	127	"	"	"	=Sb	"	55	885
"	128	"	"	"	=V	"	61	710
"	129	"	"	"	=Nb	15	59	850
"				"	=Ta	"		
				"	=Sb	"		
				"	=V	"		
Control	15	18	20	"	=Sb	62	155	150
"	16	"	22	"	=V	60	201	145

Table 5

		ZnO (mol %)	Cr_2O_3 (mol%)		$Me^{(5)}O_3$ (mol%)		R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Control	17	90	0	$Me^{(5)}$	=W	10	150	165
"	18	"	"	"	=Mo	"	165	180
Example	130	89.9	0.1	"	=W	"	71	775
Example	131	89.9	0.1	$Me^{(5)}$	=Mo	10	68	820
"	132	"	"	"	=Te	"	62	885

Table 5-continued

		ZnO (mol %)	Cr_2O_3 (mol%)	$Me^{(5)}O_3$ (mol%)			R_{25} (0%RH) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
"	133	"	5.0	"	=W	15	21	1620
"	134	"	"	"	=Mo	"	18	1815
"	135	"	"	"	=Te	"	16	1930
"	136	"	"	"	=W	5	14	2020
				"	=Mo	"		
				"	=Te	"		
"	137	60	10	"	=W	30	0.45	8775
"	138	"	"	"	=Mo	"	0.32	9610
"	139	"	"	"	=Te	"	0.21	10330
"	140	"	"	"	=W	15	0.30	9701
				"	=Mo	"		
"	141	"	"	"	=Mo	"	0.26	9910
				"	=Te	"		
"	142	30	20	"	=W	50	24	1425
"	143	"	"	"	=Mo	"	36	1305
"	144	"	"	"	=Te	"	39	1230
"	145	"	"	"	=W	20	21	1500
				"	=Mo	"		
				"	=Te	10		
"	146	20	20	"	=W	60	72	835
"	147	"	"	"	=Mo	"	88	720
"	148	"	"	"	=Te	"	69	980
Control	19	18	20	"	= W	62	130	200
"	20	"	22	"	=Te	60	145	185

Table 6

		ZnO (mol %)	Cr_2O_3 (mol%)	The third metal oxide (mol%)		R_{25} (mol%) (MΩ)	R_{25}(0%RH)/ R_{25}(100%RH)
Example	149	60	10	$Me^{(1)}$=Li	15	0.56	8950
				$Me^{(2)}$=Mg	"		
"	150	"	"	$Me^{(1)}$=K	"	0.75	9234
				$Me^{(3)}$=Zr	"		
"	151	"	"	$Me^{(1)}$=Na	"	0.38	11095
				$Me^{(4)}$=V	"		
"	152	"	"	$Me^{(1)}$=Li	"	0.43	9020
				$Me^{(5)}$=Te	"		
"	153	"	"	$Me^{(2)}$=Co	"	0.82	6305
				$Me^{(3)}$=Ti	"		
"	154	"	"	$Me^{(2)}$=Ba	"	0.51	9013
				$Me^{(4)}$=Nb	"		
"	155	"	"	$Me^{(2)}$= Sr	"	0.35	9500
				$Me^{(5)}$=Te	"		
"	156	"	"	$Me^{(3)}$=Ge	"	0.68	7750
				$Me^{(4)}$=Sb	"		
"	157	"	"	$Me^{(3)}$=Ti	"	0.52	8028
				$Me^{(5)}$=W	"		
"	158	"	"	$Me^{(4)}$=V	"	0.65	7520
				$Me^{(5)}$=Mo	"		
"	159	"	"	$Me^{(1)}$=Li	10	0.59	8210
				$Me^{(2)}$=Pb	"		
				$Me^{(3)}$=Ti	"		
"	160	"	"	$Me^{(1)}$=K	"	0.50	7845
				$Me^{(2)}$=Ca	"		
				$Me^{(4)}$=Nb	"		
Example	161	60	10	$Me^{(1)}$=Na	10	0.48	10095
				$Me^{(2)}$=Cd	"		
				$Me^{(5)}$=W	"		
"	162	"	"	$Me^{(1)}$=Cu	"	0.53	8895
				$Me^{(3)}$=Zr	"		
				$Me^{(4)}$=Ta	"		
"	163	"	"	$Me^{(1)}$=Rb	"	0.43	9427
				$Me^{(2)}$=Mn	"		
				$Me^{(3)}$=Te	"		
"	164	"	"	$Me^{(1)}$=Li	"	0.50	9113
				$Me^{(4)}$=Nb	"		
				$Me^{(5)}$=Mo	"		
"	165	"	"	$Me^{(2)}$=Co	"	0.73	7520
				$Me^{(3)}$=Zr	"		
				$Me^{(4)}$=Ta	"		
"	166	"	"	$Me^{(2)}$=Ba	"	0.55	7940
				$Me^{(3)}$=Ti	"		
				$Me^{(5)}$=W	"		
"	167	"	"	$Me^{(2)}$=Sr	"	0.53	8140
				$Me^{(4)}$=V	"		
				$Me^{(5)}$=Te	"		
"	168	"	"	$Me^{(3)}$=Ti	"	0.49	8098
				$Me^{(4)}$=Ta	"		
				$Me^{(5)}$=Mo	"		
"	169	"	"	$Me^{(1)}$=Li	10	0.62	7875
				$Me^{(2)}$=Ba	"		
				$Me^{(3)}$=Ti	5		
				$Me^{(4)}$=V	"		

Table 6-continued

		ZnO (mol %)	Cr_2O_3 (mol%)	The third metal oxide (mol%)		R_{25} (mol%) (MΩ)	$R_{25}(0\%RH)/R_{25}(100\%RH)$
Example	170	60	10	$Me^{(1)}$=Cu	10	0.57	8541
				$Me^{(2)}$=Sr	"		
				$Me^{(3)}$=Zr	5		
				$Me^{(5)}$=Te	"		
"	171	"	"	$Me^{(1)}$=Na	10	0.41	10280
				$Me^{(2)}$=Ca	"		
				$Me^{(4)}$=Ta	5		
				$Me^{(5)}$=W	"		
"	172	"	"	$Me^{(1)}$=K	10	0.53	8609
				$Me^{(3)}$=Mn	"		
				$Me^{(4)}$=Nb	5		
				$Me^{(5)}$=Mo	"		
"	173	"	"	$Me^{(1)}$=Li	10	0.69	7840
				$Me^{(3)}$=Zr	"		
				$Me^{(4)}$=V	5		
				$Me^{(5)}$=W	"		
"	174	"	"	$Me^{(1)}$=Na	10	0.74	9860
				$Me^{(2)}$=Ba	5		
				$Me^{(3)}$=Ti	"		
				$Me^{(4)}$=Sb	"		
				$Me^{(5)}$=Te	"		

What we claim is:

1. A moisture sensitive element formed of an oxide complex semiconductor comprising 89.9 to 20 mol% of ZnO, 0.1 to 20 mol% of Cr_2O_3 and 10 to 60 mol% of at least one of the third metal oxides selected from the group consisting of Li_2O, Na_2O, K_2O, Rb_2O, Cu_2O, BaO, SrO, CaO, PbO, MnO, NiO, CoO, MgO, CdO, CuO, FeO, BeO, TiO_2, GeO_2, ZrO_2, MnO_2, TeO_2, SnO_2, SiO_2, CeO_2, ThO_2, HfO_2, Nb_2O_5, Ta_2O_5, Sb_2O_5, V_2O_5, WO_3, MoO_3 and TeO_3.

2. A moisture sensitive element according to claim **1** wherein the third metal oxide is the oxide of the monovalent metal selected from the group consisting of Li_2O, Na_2O, K_2O, Rb_2O, Cu_2O and mixtures thereof.

3. A moisture sensitive element according to claim **1** wherein the third metal oxide is the oxide of the divalent metal selected from the group consisting of BaO, SrO, CaO, PbO, MnO, NiO, CoO, MgO, CdO, CuO, FeO, BeO and mixtures thereof.

4. A moisture sensitive element according to claim **1** wherein the third metal oxide is the oxide of the tetravalent metal selected from the group consisting of TiO_2, GeO_2, ZrO_2, MnO_2, TeO_2, SnO_2, SiO_2, CeO_2, ThO_2, HfO_2 and mixtures thereof.

5. A moisture sensitive element according to claim **1** wherein the third metal oxide is the oxide of the pentavalent metal selected from the group consisting of Nb_2O_5, Ta_2O_5, Sb_2O_5, V_2O_5 and mixtures thereof.

6. A moisture sensitive element according to claim **1** wherein the third metal oxide is the oxide of the hexavalent metal selected from the group consisting of WO_3, MoO_3, TeO_3 and mixtures thereof.

7. A moisture sensitive element according to claim **1** wherein said semiconductor comprises 80 to 30 mol% of ZnO, 5 to 20 mol% of Cr_2O_3 and 15 to 50 mol% of the third metal oxide.

8. A moisture sensitive element according to claim **7** wherein said semiconductor comprises 60 mol% of ZnO, **10** mol% of Cr_2O_3 and 30 mol% of the third metal oxide.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,926,858 Dated December 16, 1975

Inventor(s) Noboru ICHINOSE et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE TITLE PAGE:

Please change the priority date of Japanese Application No. 48-78478 in the Foreign Application Priority Data from "Aug. 13, 1973" to--July 13, 1973--

Signed and Sealed this

thirteenth **Day of** *April 1976*

[SEAL]

Attest:

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