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Gas-Surface Interaction Influence on Electrical Properties of New Gas Sensitive Metal Oxide-Metal Sandwich Structure

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The novel sandwich structure based on insulating metal oxide top-layer (SnO_2) and an ultra thin metal (Pt) bottom-layer is proposed. The resistance switching effect induced by CO gas is obtained in these sandwich structures. The effect is proved being originated by properties of the ultra thin Pt film. The large amplitude of the effect is related to the tin oxide top-layer. Some features of the switching effect are discussed on the basis of the model proposed.

1. INTRODUCTION

The semiconducting gas sensors are mostly based on the metal oxide resistors[1-3] or the field effect transistors (ChemFET)[4,5]. These sensors are mainly used for gas sensor arrays because the gas sensing parameters and the methods of an improvement of the parameters are widely studied[1-5]. However, the development of a new type of gas sensors compatible with the silicon planar technology could be attractive and prospective. Moreover an application of well known gas sensing principles in more sophisticated semiconducting structures could be related with qualitatively different possibilities in gas sensor development.

In our report we are discussing the novel sandwich structure based on an insulating metal oxide top-layer and an ultra-thin metal bottom-layer. We introduce the experimental results of the investigation of the new gas sensitive structure. The model structure consists of two thin films of Pt and SnO_2. The resistance response to CO gas is studied at temperatures from 60 °C to 240 °C. The resistance switching dependent on CO gas concentration is obtained in ultra thin Pt films. It is experimentally demonstrated that the resistance switching effect is more distinctive in the tin oxide covered Pt films called the sandwich structures in our report.

2. BASIC MODEL

The concept of the gas sensitive sandwich structure is based on the semiconducting properties of the degenerated bottom-layer and on the gas controlled phenomena in the metal oxide-metal interface. The band bending near the surface of the bottom-layer leads to an increase of electron potential energy because of negative surface charge. It means that the degeneracy of semiconductor disappears in the depletion region in the bottom-layer. In ultra-thin films the cross-section of the conductive channel parallel to the surface is determined by the difference between the film thickness and the length of depletion region. Since an electric conductivity of degenerated part of the film differs significantly from that of the depletion region, the electric conductivity of the film are controlled only by degenerated part of the film. Taking into account that the length of depletion region depends on the excess surface charge, it is evident that the cross-section of the degenerated channel is dependent on gas chemosorption. The most significant effect of gas chemosorption on conductivity could be expected when the thickness of the film is nearly equal to the length of depletion region.

It could be assumed two possible phenomena controlling electron potential energy in the interface between top- and bottom-layers. First, gas species chemosorbed on the surface of the top-layer diffuse toward the interface and originate point defects in the interface. Because of electron trapping by the defect states, an excess interface charge should modify cross-section of degenerated channel. Second is related to electric field effect originated by excess surface charge on the top-layer. In this case the surface charge is supposed modifying electron potential energy in the interface region because the Debye screening length is approximately equal to thickness of the top-layer. It means that the depletion region nearly penetrates the top-layer.

3. EXPERIMENTS

Two types of samples were prepared for our study. First, ultra-thin Pt film were sputtered from Pt target in pure Ar atmosphere. The thickness of the films were altered by the change of sputtering time. The films were characterized by the sheet resistance R^*_{Pt} obtained at the room temperature just after growth. Second type of samples are called sandwich in this report. The sandwich consists of too layers: ultra thin bottom-layer and tin oxide top-layer. The top layer was sputtered by dc-magnetron from metallic tin target. Tin oxide film is obtained due to oxidation of tin in atmosphere of $Ar:O_2$ = 4:6 during the sputtering. The bottom layers of different thickness of Pt were covered with practically similar top layer. Glass or silicon plate with insulating SiO_2 layer were used as substrates in both cases.

The resistance response of all the samples to CO gas was tested in the chamber with the air which room humidity was approximately 45%. In all cases the temperature was varied from 80 °C to 240 °C. During the response measurements a fixed amount of contaminating CO gas was injected into the chamber.

4. RESULTS AND DISCUSSIONS

We obtained anomalous resistance decrease of the sandwich in the air contaminated with CO gas. The resistance response to CO gas could be characterized as switch of the resistance from low response state to high response state. The results are illustrated in Fig. 1 by typical dependencies of sheet resistance versus CO concentration in the air. The results are obtained at two working temperatures in the sandwich based on the Pt film which thickness is nearly optimum (R^*_{Pt}≈2.4 kohm per square). One can distinguish the small response state (the uper part of the dependence) and the high response state (after steep decrease of the resistance) in Fig. 1.

The resistance of the sandwich R_{sdw} is slightly CO concentration dependent in the small response state (see results at T=180 °C when CO is less then 450 ppm). On the other hand R_{sdw} is constant in high response state. The difference in the concentration between the two states is approximately equal to 40 ppm. The critical concentration at which the switching is detected depends clearly on the working temperature.

It should be pointed out however an extremely high sensitivity to CO gas of the sandwich when compared with that of the Pt film (compare Figs. 1 and 2).

The resistance response to CO gas of the Pt film are plotted in Fig. 2. The results in Fig. 2 illustrate the influence of the initial resistance of the Pt films R^*_{Pt} (or thickness) on resistance response to CO gas. Since decreasing resistance R^*_{Pt} means increase of film thickness, it could be deduced from the results in Fig. 2 that critical thickness could be found separating the CO sensitive Pt films from that insensitive. Moreover the critical thickness depends on concentration of CO gas in the air. It could be seen in Fig. 2 that the contamination of the air with 60 ppm of CO gas is detected only by thin Pt films when R^*_{Pt} > 2.4 kohm per square. In contrast to this greater amount of CO gas (say 400 ppm) is detected by thicker films which R^*_{Pt} > 1.4 kohm per square. So the critical thickness

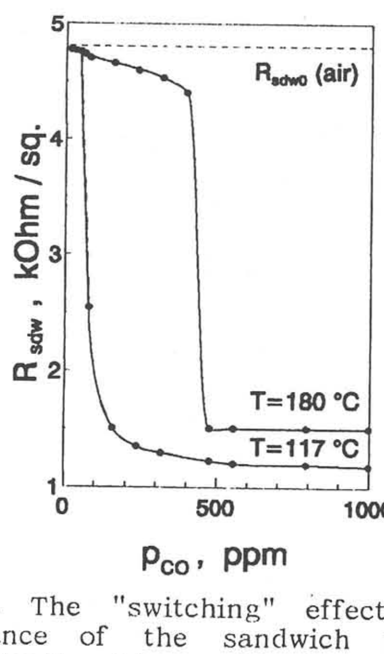

Fig. 1.. The "switching" effect: sheet resistance of the sandwich vs. CO concentration at two working temperatures.

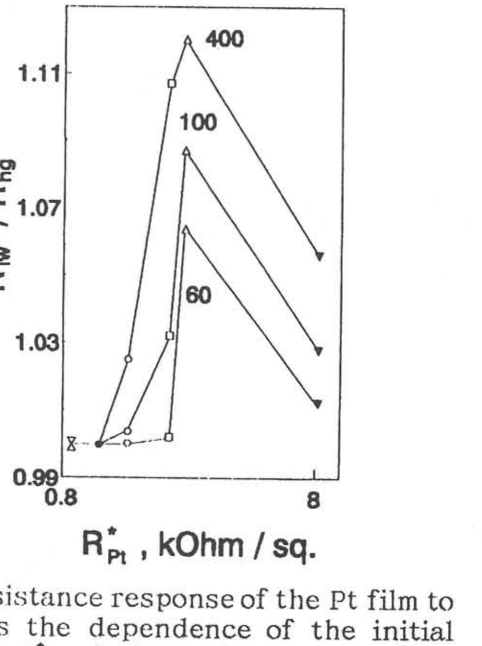

Fig. 2. Resistance response of the Pt film to CO gas as the dependence of the initial resistance R^*_{Pt} of the Pt film. Numbers at curves represent CO amount in ppm.

for CO sensitive Pt films increases with increasing amount of CO gas in the air. However it should be noted that very thin Pt films are also insensitive to CO gas as these very thick. This fact could be illustrated by the decrease of the resistance response of the Pt films with R^*_{Pt} approaching 8 kohm per square (see Fig. 2).

The results in Fig. 2 could be explained qualitatively on the basis of our model. As it follows from our model, thin films are insensitive to gas when the length of depletion region exceeds thickness of the film. On the contrary to this, films of significant thickness are independent on exposure to gas because cross-section of the degenerated channel is much greater then the length of depletion region. Hence small

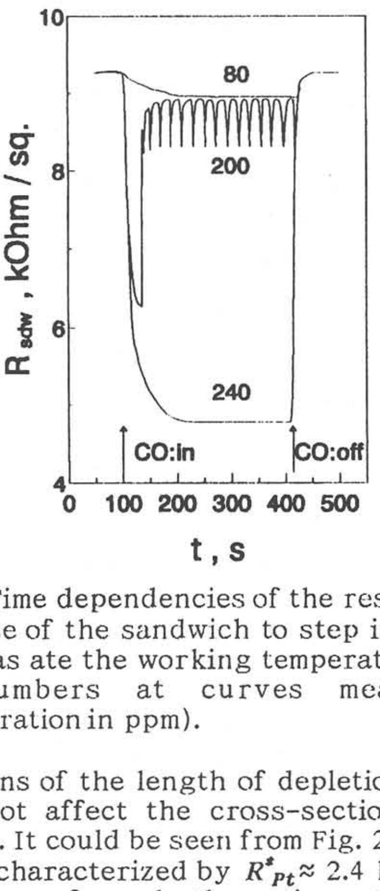

Fig. 3. Time dependencies of the resistance response of the sandwich to step increase of CO gas ate the working temperature 168 °C (numbers at curves mean CO concentration in ppm).

variations of the length of depletion region could not affect the cross-section of the channel. It could be seen from Fig. 2 that the Pt film characterized by $R^*_{Pt} \approx 2.4$ kohm per square are of nearly the optimum thickness for CO gas detection. It means that the degenerated channel is narrow enough to be controlled precisely by the change of the surface charge density.

The typical responses of the sandwich to a step increase of CO concentration up to three different values are shown in the Fig. 3. The two response states are also determined by these time dependencies of the response. Two traces of the time dependence are found being unchangeable in two wide regions of CO concentrations. The first one is marked by CO concentration equal to 80 ppm. The same trace (80 ppm in Fig. 3) is obtained for the response to CO concentrations below 190 ppm. Whereas the time dependencies of the response to CO concentration exceeding 240 ppm are the same as the trace marked by 240 ppm in Fig. 3.

The oscillations are detected at CO concentrations from the range 190 - 240 ppm in the sandwich resistance response to CO gas (see trace marked by 200 ppm in Fig. 3). Analogous oscillations were obtained in the vicinity of the critical CO concentration at all working temperatures and in the samples with the Pt films of different thickness.

5. CONCLUSIONS

In the present report we propose the model sandwich structure consisting of ultra thin Pt bottom-layer and tin oxide top-layer. Anomalous resistance response to CO gas is obtained experimentally in these sandwich structures. The response is characterized by extremely steep decrease of the sandwich resistance in response to a critical CO concentration. The critical CO concentration increases with the rise of the working temperature. These steep changes of the sandwich resistance are named as CO induced switching effect. The effect is proved being the characteristic property of the ultra thin Pt film. Whereas an extremely large amplitude of the switching effect is proved being originated by tin oxide top-layer.

6. REFERENCES

1) K.D.Schierbaum, U.Weimar and W.Gopel. Sensors and Actuators B, 7 (1992) 709.
2) K.D.Schierbaum, J.Geiger, U.Weimar and W.Gopel. Sensors and Actuators B, 13 (1993) 143.
3) G.Gaggiotti, A.Galdikas, S.Kačiulis, G.Mattogno, A.Šetkus. J.Appl.Phys., 76 (1994) 4467.
4) H.Sundgren and I.Lundstrom. Sensors and Actuators B, 9 (1992) 127.
5) I.Lundstrom, C.Svensson, A.Spetz, H.Sundgren and F.Winquist. Sensors and Actuators B, 13-14 (1993) 16.