ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Study of Adsorption and Desorption 0f Gas on Semiconductor Layers.

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ABSTRACT

The presence of a foreign element on the surface of a semiconductor material may be indicated by an adsorption which can lead to a change in the surface electric conduction. This property is closely related to the nature and conditions of preparation and treatment of the material. We have elaborated the ZnO oxide layers by the vacuum evaporation technique of zinc layers on different substrates and then made their thermal oxidation in oxygen at 450°C. The adsorption and desorption of oxygen at different temperature, create significant variations in the electrical resistance R of the sample. The isotherm desorption made at the same temperatures show that the adsorption layer can be regenerated but for relatively long periods. In case of failure, the samples are subjected to temperature programmed desorption by scanning the temperature at relatively low speed of 3°C/mn.

Keywords: gas sensors, semiconductor surface, adsorption / desorption, reducing gases.

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ISSN: 0975-8585

INTRODUCTION

The growing interest and requirements of high technology, particularly in microelectronics have led to the necessity of using semiconductor materials in thin layers. Notably, the properties of such materials are significantly affected by surface phenomena.

The surface may be regarded as a separation boundary between the volume of the material and the surrounding medium. It presents itself as the headquarters of many physical and chemical reactions. Indeed, the surface atoms have unsatisfied bonds that enable them to retain foreign particles. During the approach to the surface, the particle passes through a series of steps beginning with adsorption. The final step is the definitive fixation of the particle on the surface.

The particles of the surrounding environment in the vicinity of the surface, at distances of the order of the interatomic distance, can get caught on surface sites. Depending on the nature of the particle, pressure, temperature and the occupied site, the coupling is stronger or weaker. This notion of adhesion is the basis of many physico-chemical phenomena in which particles interact with surface atoms.

Two processes will combine when one puts a semiconductor layer in the presence of a reactive gas. A process of physical adsorption (physisorption) and chemical adsorption process (chemisorption) may occur by interaction with gas molecules.

In order to implement experimentally the adsorption and desorption of gases on semiconductor surfaces, we thought to develop layers of zinc oxide and we chose to use oxygen as the more active element in the air. The zinc oxide is characterized by a behavior of the semiconductor n-type wide band gap.

Theory

In the simple case, one can say that the gas while being fixed on a semiconductor surface introduces into the forbidden band of the material a surface state which can play the part of acceptor or donor of electrons: if it is acceptor the surface takes a negative electric charge, while if it is donor it takes a positive electric charge. This surface charge must be compensated under the semiconductor surface by a zone of space charge of opposite sign whose nature (accumulation, impoverishment), depends on type *n* or *p* of the semiconductor. The space charge modifies the conductance of the surface zone of the solid and consequently the total resistance of the semiconductor plate. Note that the relative variation of resistance for a single-crystal layer of a semiconductor of the type *n* is given by [1]:

$$\frac{R}{R_0} = \frac{1}{1 - qKR_0\mu_n N_A^-} \qquad (1)$$

Where R_0 is initial electric resistance, q the electronic charge, μ_n the mobility of the electrons, varies and *K* a dimensional constant of the layer. N_A^- varies according to time during isothermal adsorptions and desorptions until electronic equilibrium is reached in **both** cases.

We will use then, the resistance variation with the temperature and time as a parameter of gas interaction.

EXPERERIMENT

The used materials

In this work, we are interested in studying the behavior of surface layer material polycrisatallin ZnO. It is a semiconductor of n-type with relatively large gap of 3.2 eV. This compound is characterized by deviations from stoichiometry, responsible nature semiconductor [2-5].

Elaboration of layers

The used layers of zinc oxide ZnO were prepared by oxidation at 450 ° C under oxygen O_2 during 2:00 to 4:00 hours, thin layers of Zn. These layers were prepared by evaporation under vacuum (10^{-6} Torr) (conventional evaporator metals) on metal substrates glass and alumina.

Installation of electrical measurements

Electrical measurements were carried out in a suitable experimental setup. It consists essentially of a housing of stainless steel equipped with a sample holder and in which it is possible to create a high vacuum. The electrical contacts, ohmic verified in the field of working temperature (20° C to 350° C) are taken on the surface, or with the aid of silver lacquer or pressure measurement were taken on the surface by screws installed on the sample holder for this purpose.

RESULTS AND DISCUSSION

Electrical measurements of the considered layers of zinc oxide are considered taken between two points on the ends of these surface layers, as a function of temperature and time, and vacuum being adsorptions and desorptions oxygen.

The maximum working temperature was set at T_{max} = 350 ° C to avoid decomposition of the substrates and alteration of contacts for zinc oxide. The magnitude of the electrical resistance of the layers of zinc oxide, measured at room temperature under vacuum in the dark is of the order of a few tens of KΩ

Variation of the resistance electrical during a temperature rise

This operation consists in measuring the value of the electrical resistance R under a dynamic vacuum of 10^{-6}mb at fixed values of the temperature in the range from ambient to 350 ° C. Arrhenius curve Log R = f (10^3 / T (K)) obtained is linear, characteristic behavior of semiconductor(figureIV.1).

ISSN: 0975-8585

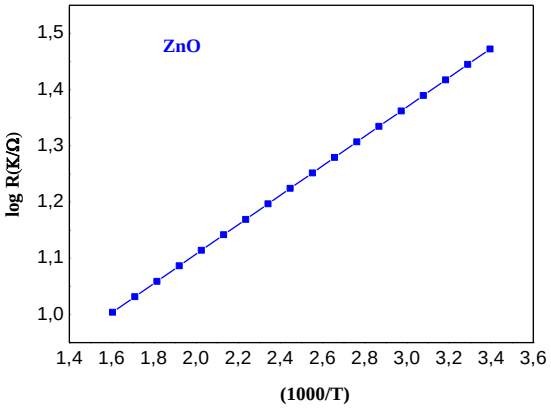

Figure IV.1: The curve LogR=f(10^3/T(K)) of ZnO layer Zn Ocouche de

Adsorptions and desorption isotherms of oxygen

We conducted experimental tests of adsorptions and desorption of oxygen on a layer of zinc oxide. These tests were performed at temperatures of adsorption Ta equal to 113 ° C and 131 ° C. Adsorption times are limited to 3 minutes to avoid possible releases of gas atoms in the network of the material.

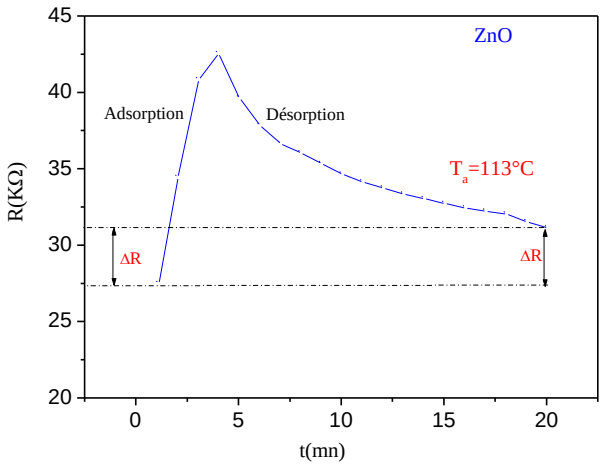

Figure IV.2: Variation of resistance with time during an adsorption-desorption of oxygen on sample of ZnO at Ta=113 ° C

The curves in Figures IV.2 and IV.3 show that during the isothermal adsorptions of oxygen at temperatures Ta, the electrical resistance R of the layer increases with time. Indeed, the ZnO has a behavior of a semiconductor n-type. The valence of oxygen makes that this element acts as electron acceptor. Thus, the oxygen gas in contact with the surface of the ZnO layer at a temperature Ta is adsorbed on the surface sites by trapping electrons network becomes negatively charged and forming a negative surface layer on the surface. This electron trapping decreases the concentration of the conduction electrons in the region of space charge ZCE depleted below the surface.

ISSN: 0975-8585

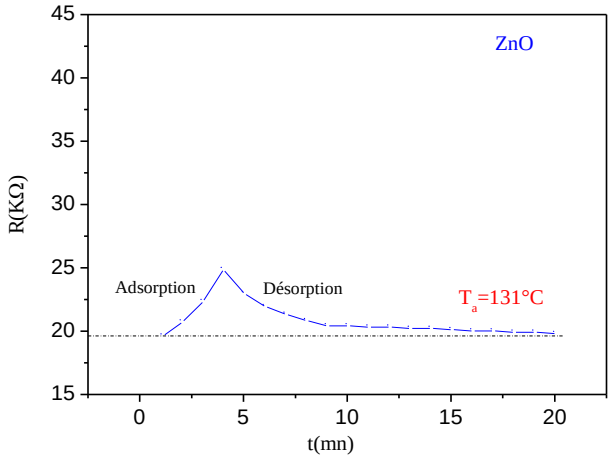

Figure IV.3: Variation of resistance with time during an adsorption - desorption of oxygen on sample of ZnO at T_a = 131 ° C.

This space charge is more important than the ionosorbed oxygen density is great. The latter increases with time and may, in some cases, reach a state of equilibrium. The formation of a depleted zone of space charge explains the increase in strength during the oxygen adsorption. The gradual increase in the density of ionosorbed states time makes ZCE largest and increases R. From the results we can see that the increase of R after 3 minutes adsorption depends on the temperature Ta. Desorption isotherm is performed by a dynamic pump for draining oxygen from the test chamber in which a vacuum is established. Desorption is the reverse phenomenon of adsorption occurs by the release of adsorbed elements. The ionosorbed oxygen initially, return the electrons to the lattice gradually as and for his release. The concentration of conduction electrons increases again moving towards its initial value before adsorption by reducing the resistance R to its initial value. Curves of isotherm desorption performed at temperatures of 113 ° C adsorptions and 131 ° C clearly show the decrease of R. When this decrease back to its initial value R before adsorption, as in the case of Figure IV.3, the density of states is completely desorbed and restored to its original state. If after a period of desorption, even relatively long, the value of R does not reach its initial value, as in the case of Figure IV.2, the difference $\Delta R = R_{ads}-R_{des}$ represent the density of ionosorbed states still remaining. Order to desorb completely the ionosorbed density of elements, we proceed by temperature programmed desorption DTP.

Desorption Temperature Programmed ΔR-DTP

Note that when the electrical resistance of the ZnO layer does not return to its initial value R_0, desorption is incomplete. In this case, it takes additional energy to desorb the particles still remaining ionosorbed. This DTP is realized by increasing the temperature of the layer at a constant speed and slow enough to 3 ° C / min under high vacuum until the maximum temperature. To exploit this DTP, it is necessary to meet the so called reference curve obtained before adsorption in the same conditions as DTP. At the DTP layer passes by progressive values of energy provided by the temperature and for the times when it reaches the energy equivalent to the ionosorption ionosorbed particles are desorbed and the resistance drops to its initial value corresponding to the same temperature. This decrease in

ISSN: 0975-8585

R is denoted by ΔR-DTP. The curve in Figure IV.4 is a ΔR-DPT a layer of ZnO carried out after adsorption and desorption isotherms at Ta = 113 ° C. It is noted that the gap between the two ΔR-DPT curves and reference decreases as the temperature increases until the two curves meet to high temperatures showing the complete desorption of the layer by this technique

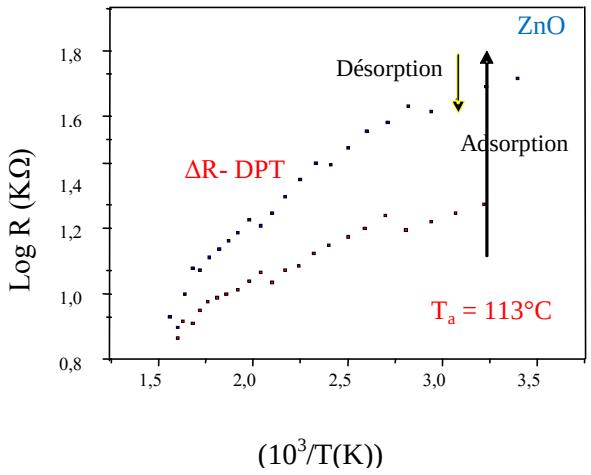

Figure IV.4: Variation of resistance during treatment ΔR-DTP at Ta = 113 ° C (Desorption Temperature Programmed).

Application of adsorption

The solid materials present surface states which can be active against of chemical elements in contact with the surface. This surface reactivity result to the solid surface where multiple reactions can occur between the material and the environment. Some physicochemical surface reactions can cause the change of material properties. In the case of the reactions of surface states with foreign elements lead to the formation of complex phases forming on the surface or lead to the diffusion of these elements in the volume, the material is more stable.

If the material has surface states allowing some elements to adsorb from the network without the material, desorption of these elements will be possible physicochemical reaction is reversible. In this case, the surface of this material may be used for applications in the detection of gaseous pollutants from the atmosphere.

Research in this area shows that the semiconductor layers are most appropriate for these applications. Metal oxides such as zinc oxide and tin oxide are most commonly used for their properties and stability.

CONCLUSION

This work has allowed us to study and understand the mechanisms that take place during the adsorption and desorption of a gaseous element on a semiconductor surface. The ionosorption causes the formation of a space charge region in the surface by varying the electrical surface resistance which provides information on the presence of this

ionosorbtion state or its desorption. These variations are governed by laws derived from theoretical models.

To highlight the ionosorption gas on semiconductor surfaces, we have developed layers of zinc oxide by thermal oxidation at 450 ° C for zinc coatings obtained by vacuum evaporation on glass substrates and alumina.

Arrhenius curve found in vacuum is linear, characteristic behavior of a semiconductor.

The resistance of the layer is studied is high on the order of MΩ at room temperature and in the order of kΩ at the elevated temperature. It varies with temperature.

Oxygen adsorptions performed at temperatures T_a =113°C and T_a = 131°C caused an increase in the electrical resistance of this layer showing the character of the oxygen acceptor and the nature of the semiconductor n-type ZnO

Desorption isotherm performed at the same temperatures shows that the adsorption layer can be regenerated but for relatively long periods. In case of deficiencies, the sample is subjected to a temperature programmed desorption DTP relatively slow rate of 3 ° C / min to restore the surface of the material to its original condition.

These adsorptions performed on the ZnO indicate the sensitivity of the surface of this component to elements of the environment and the possibility of its use in the field of gas sensors semiconductors.

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