HALL EFFECT MEASUREMENTS TO CALCULATE THE CONDUCTION CONTROL IN SEMICONDUCTORS FILMS OF SnO_2.

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ABSTRACT

Hall effect measurement is one of the most powerful methods for obtaining information about transport mechanisms in polycrystaline semiconductor compounds that constitute the basis for understanding the sensing function of semiconductor gas sensors.

The presence of grain boundaries represents the essential difference between single-crystal and polycrystalline semiconductors. The boundaries are important because they generally contain fairly high densities of interface states which trap free carriers from the bulk of the grains.

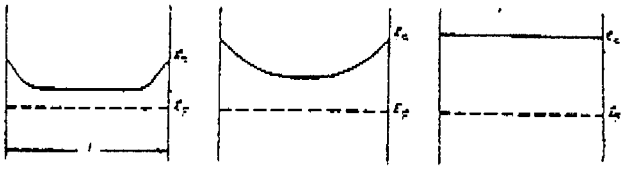
We use the grain size of semiconductor (calculated by XRGA technique [1]) and Hall effect measurements in order to obtain conduction band profiles [2,3]. Depending on the preparation method (reactive sputtering, electron beam, and serigraphy),three situations of conduction control can be distinguished. From the analysis of the material microstructure we obtain similar results.

INTRODUCTION

Hall coefficient measurement is a method for acquiring information related to carrier concentration and Hall mobility. Such measurement contributes to the understanding of conduction mechanisms in SnO_2 sensors for detecting gases, with the purpose of improving their operating characteristics, in order to obtain optime sensors attending to electrical conduction and microstructure characteristics.

In this paper, Orton and Powell [2] theory is applied in order to obtain conduction band profiles through single grains of SnO_2 semiconductors films (n-type) by three different methods.

Basically, three situations depending on the relative magnitude of n_t compared to $N.l$ and on the Debye length L_D compared to the grain size l , can be distinguished. Herein, n_t is the charge density trapped in the surface states, N the carrier number at the bulk and l the grain size (Fig.1).



(a) (b) (c)

Fig.1 Conduction band profiles of a n-type film.

a- If $n_t < Nl$, the carrier density n is constant at the bulk and the mobility is thermally activated (Fig.1a).

b- If n_t Nl, the depletion layer extends through the grain, giving the band profile shown in fig 1b, where mobility is still barrier limited. This profile occurs when $L_D < l/2$.

c- If n_t Nl but $L_D > l/2$ the conduction band will be essentially flat throughout the film. There will be no barriers to current flow and mobility will not be thermally activated (Fig.1c).

It is deduced that the grain size of sensor semiconductor films is a parameter very important to measure. The calculation was made by XRGA technique [1].

EXPERIMENTAL

The samples prepared by electron beam, serigraphy and reactive sputtering ,were thermally annealed in synthetic air at 400°C during 2-3 hours. The Hall effect measurements were carried out in Ar atmosphere, starting from room temperature till 300°C. Applying the Van der Paw method [3] we calculated the conductivity and Hall coefficient. With these values the carrier density and mobility were evaluated (tables 1,2,3).

Table 1 Tin Oxide films prepared by reactive sputtering (5 % O_2)

T (°C)	σ (Ω cm)$^{-1}$	n (10^{18} cm^{-3})	μ (cm^2 V^{-1} s^{-1})	R_H (cm^3/Cb)
25	0.88	2.71	2.03	2.31
50	1.01	2.81	2.25	2.22
100	1.24	2.93	2.65	2.13
150	1.53	3.07	3.12	2.03
200	2.31	3.89	3.71	1.61
250	2.96	4.38	4.21	1.42
300	2.98	4.68	3.97	1.33

Table 2 Tin Oxide films prepared by electron beam

T (°C)	σ(Ω cm)$^{-1}$	n(10^{17} cm^{-3})	μ (cm^{2}V^{-1}s^{-1})	R_H (cm^3/Cb)
25	0.11	2.00	3.42	31.38
50	0.12	1.38	5.25	45.36
100	0.12	1.19	6.52	52.44
150	0.12	0.64	11.96	97.80
200	0.13	1.13	7.41	55.28
250	0.17	1.69	6.32	36.85
300	0.27	0.80	20.97	77.96

Table 3 Tin Oxide films prepared by serigraphy

T (°C)	σ (Ω cm)$^{-1}$	n (10^{17}cm^{-3})	μ (cm^2/V^{-1}s^{-1})	R_H (cm^3/Cb)
25	0.67	0.43	96.5	140.62
50	1.43	1.12	79.8	50.58
100	3.73	7.01	33.2	8.90
150	9.48	11.20	52.9	5.60
200	15.30	18.80	50.8	3.30
250	28.51	8.70	204.6	7.10
300	64.63	7.34	549.6	8.50

RESULTS

The L_n [1] may be written:

$$L_n=(\in kT/nq^2)^{1/2} \qquad (1)$$

k being the Boltzman constant, $\in$ the permitivity and q the electric charge. For the three types of samples prepared L_n changes with the temperature (table 4)

Table 4 Modification of L_D with temperature for SnO_2 films prepared by reactive sputtering, electron beam and serigraphy

T(°C)	L_D(Å)	L_D(Å)	L_D(Å)
25	26.6	97.8	211
50	27.2	122.6	137
100	28.6	141.8	58.5
150	29.7	193.7	49.3
200	27.9	163.9	40.2
250	27.7	140.9	62.2
300	28.0	214.4	70.8

For calculating the band-bending ,Φ_b ,we apply [2]:

[illegible] being μ the mobility (2)

knowing that $\Phi_b = q^2 n_t^2 / 8\in n$ (3)

we calculated the values of N (estimate like carrier number calculated from Hall effect measurements) and *l* (grain size). We compared n_t values and N.*l* for each film type (tables 5,6 and 7).

Table 5: Comparison between n_t values and N.*l* for SnO_2 films prepared by reactive sputtering, table 6: same as table5 ,by electron beam and table 7: same as table 6, by serigraphy.

n_t (10^{12})	N.*l* (10^{12})	n_t (10^{11})	N.*l* (10^{11})	n_t (10^{12})	N.*l* (10^{12})
2.55	0.95	8.73	10.0	0.42	0.43
2.59	0.98	7.25	6.9	0.65	1.12
2.64	1.03	6.73	6.0	0.67	7.01
2.70	1.08	4.93	3.2	2.12	11.20
3.04	1.36	6.56	5.7	2.74	18.80
3.23	1.53	8.03	8.5	1.86	8.70
3.34	1.64	5.52	4.0	1.71	7.34

Table 5 **Table 6** **Table 7**

The grain size of films prepared by reactive sputtering is ≈ 60Å. In general, it was observed, that $L_D \approx l/2$ and $n_t \approx N.l$ for whatever temperature. This type of films can be associated to case (b) as well as to (c) (fig.1). Temperature have more influence on the carrier number. The films prepared by electron beam correspond better to case (b) (fig.1). The films prepared by serigraphy associate to case (a) (fig.1). Here the mobility is thermally activated and grain boundaries control the conduction.

Relating the Orton and Powell theory with film microstructure [1], we can distinguish three cases depending on the relative magnitude of *l* and L (L being the space charge layer). This situation is graphically demonstrated in fig.2.

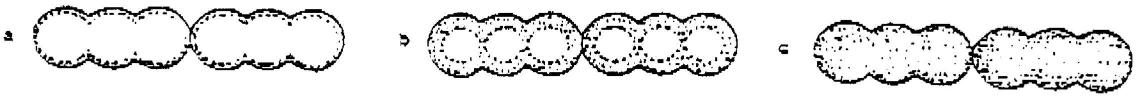


Fig.2 A model accounting for the grain size effects. a) l»2L, b) l≥2L, c) l<2L

The thickness of the space charge layer is related to Debye length (L_D) usually by:

$$L=L_D(2eV_s/kT)^{1/2}$$

where eV_s is the surface potential and kT is the thermal energy.
a- l»2L grain boundary control , b- l=2L neck control and c- l<2L grain control.

1- For films prepared by reactive sputtering:
$L_D \approx 30$ Å , L = 40 Å , l = 60 Å : case c.

2- For films prepared by electron beam:
$L_D \approx 150$-200 Å , L = 300 Å , l = 500 Å : intermediate case between a and b.

3- For films prepared by serigraphy:
$L_D \approx 70$ Å , L = 120 Å , l 1000 Å : case a.

DISCUSSION AND CONCLUSIONS

Comparing Orton and Powell theory with the microstructure model we can establish that:

- In films prepared by reactive sputtering (thin films) the electronic conduction is carried out in the whole grain; electron transport at any place inside the particle becomes sensitive to superficial effects. Sensor sensibility depends on grain size.

- In films prepared by electron beam, the conduction control is performed partly by necks and partly by grain boundaries. These films are intermediate between thick films and thin films with low crystallinity degree.

- In the films prepared by serigraphy (thick films) the conduction control is carried out by grain boundaries. The resistance at the grain boundary contacts determines the whole resistance, thus giving rise to gas sensitivity independent of grain size.

The three aforementioned cases, revealed that the way of preparation of the sensor material is fundamental, as the microstructure is a factor that determines the sensibility. Considering the microstructure, the conduction control is different. Hence, due to that reason, the detection mechanisms differ also.

References

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