JOURNAL OF MATERIALS SCIENCE **34** (1999) 4661–4664

Fabrication of piezoelectric thin film of zinc oxide in composite membrane of ultrasonic microsensors

J. GOLĘBIOWSKI
Institute of Theoretical Electrotechnics, Metrology and Materials Science, Technical University of Łódź, Poland
E-mail: jacekgol@ck-sg.p.lodz.pl

The fabrication of the thin piezoelectric layers on the silicon substrate by means of the pulse dc and the dc magnetron sputtering methods is discussed. The influences of the different kind of the surface, the conditions of deposition as well as the process of the thermal stabilising on the properties of the piezoelectric layer were investigated. The results of the investigations of the diffraction spectrum for the thin ZnO films are presented and discussed. The selection of the technological process parameters for the production of the thin ZnO layers in the sensor membranes with the ultrasonic wave generated was analysed. © *1999 Kluwer Academic Publishers*

1. Introduction

The most common sources of the ultrasonic waves in the membrane microsensors are the piezoelectric transducers. The IDT—interdigital transducers consist of the metallic belt electrodes overlaid on the piezoelectric surface. These transducers are used to the generation and detection of the plate waves [1, 2]. The simplified construction of the membrane sensor is shown in Fig. 1. The ultrasonic waves, plate type are generated and propagate in the thin composite membranes. The main elements of the membrane are (Fig. 1): the crystalline silicon (Si) which is an elastic layer, then the piezoelectric layer, i.e., zinc oxide (ZnO) and the metallic electrodes of the IDT transducers which are made of aluminium (Al) [3]. The layer of the silicon nitride (Si_3N_4), or the silicon oxide (SiO_2) can be used instead of the silicon layer. The one of the most common piezoelectric material used is ZnO which has excellent piezoelectric properties for the thin layers, and the one of the method of overlaying is the magnetron sputtering method.

2. The conditions of the ZnO layer deposition

The selections of the deposition conditions as well as the material of the basis are essential in order to obtain a ZnO layer which has good piezoelectric properties [4] and the low internal tensions [5]. The methods of the piezoelectric ZnO layers' production which are overlaid on the non-piezoelectric substrates and have quite large thickness are known i.e., in the sensors with the surface waves (SAW) [6, 7]. However, for the sensors with the thin membranes, i.e., the membranes which thickness is comparable with the thickness of the ZnO layers, the layers have to have good piezoelectric properties and introduce minimal internal tensions. The magnetron sputtering method allows to obtain thin regular layer of ZnO which has good piezoelectric parameters [8]. It is possible to use the target in a form of pure zinc or zinc oxide, analytical grade. Depending on the kind of the material the suitable composition of the gases is used: for the zinc oxide cathode the argon is applied, whereas for the zinc cathode the mixture of the oxygen and argon is used. For the membrane sensors with ultrasonic waves thin, piezoelectric layers are polycrystalline layers. It is extremely important to obtain suitable orientation of the crystalline structure, i.e., *c*-axis normal to film surface. These films characterise high resistivity and they have a strong piezoelectric effect. In the magnetron sputtering method one should use the proper pressure of gases in the chamber as well as keep the proper ground temperature. The important parameters are the density of power that is emitted on the cathode and the distance between the target and the ground; these factors vitally influence the ratio of the ZnO layer deposition. The distance and the location of target in the relation to the ground will influence regularity of the ZnO film deposition.

In the process of the thin ZnO layer production one should take into consideration the influence of the ground properties, especially its crystalline structure. For sensor membranes which are made on the basis of crystalline silicon this factor has important significance because the orientation of the silicon crystalline lattice in relation to the membrane surface strongly influences the structure of the polycrystalline piezoelectric layer [9–11]. In the sensor membranes besides the layers which have isotropic properties (Si), the anisotropic layers can also exist, i.e., SiO_2 or Si_3N_4. The order of the deposited layers as well as their thickness and structure

0022–2461

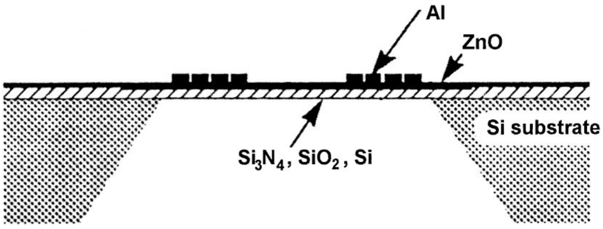

Figure 1 The cross section of the sensor membrane with the ultrasonic plate waves. Al—aluminium electrodes of IDT, ZnO—piezoelectric film of zinc oxide, Si_3N_4, SiO_2 or Si—elastic layer.

influence the piezoelectric properties of the ZnO film obtained [12]. The membrane microsensors are produced on the basis of crystalline silicon. The basic materials were plates with diameter of 76.2 mm (3 in.) made of monocrystalline silicon with thickness of 380 μm one-sidedly polished. The rectangular membranes can be obtained in the process of etching of the anisotropic silicon, $\langle 100 \rangle$ orientation. That is why the $\langle 100 \rangle$ silicon orientation was used to the further investigations.

Using the magnetron sputtering method the ZnO films were obtained for the different grounds (Table I) and for the following variable working conditions—the change of the gas mixture composition, directly current work (dc) and the pulse current work with the frequency of 5 kHz (pulse dc) and for different times and different speeds of deposition:

1. The gas mixture compositions: 50% O_2 + 50% Ar or 100% O_2,
2. DC work or pulse dc magnetron sputtering,
3. The variation of the time and the speed of deposition. As the results the thickness "h" of the ZnO layers were in the range 0.8–2.7 μm. (Table II).

The other conditions for the ZnO deposition by the magnetron sputtering method (Table II):

TABLE I The grounds the ZnO layers were produced

Ground	Glass corning 0211	Si $\langle 100 \rangle$ (μm)	Si_3N_4 (μm)	BSG (μm)	Al (μm)	Cr (μm)
a	a	—	—	—	—	—
b	—	12	—	—	1	—
c	—	12	0.1	—	—	—
d	—	12	—	—	—	0.15
e	—	12	—	2.1	—	—

[a]BSG-silicon oxide with the addition of boron (B).

1. The power for the cathode 100–200 W,
2. The power density "P" at the cathode 2–4 W/cm^2,
3. The current density for the magnetron cathode 0.01–0.02 A/cm^2,
4. The composition of the gas mixture: 50%O_2 + 50%Ar, 100%O_2,
5. The pressure "p_1" during of deposition 5–10 Pa,
6. The temperature "T_1" of ground 200°–250 °C,
7. The time "t_1" of the deposition depending on the film thickness,
8. The time "t_2" of warming 0–6 h (h),
9. The time of cooling down 100 °C about 1 h,
10. The warming temperature "T_2" 300°–350 °C,
11. The pressure "p_2" during the warming 0.01–0.02 Pa,
12. The deposition rate 0.1–0.5 nm/s,
13. The target purity Zn 99.99.

As a reference material the glass Corning 0211 type, was used.

The silicon film was the basic layer for the other films; metallic layers (Al, Cr) or the amorphous layers (Si_3N_4, SiO_2).

3. The diffraction characteristics of the spectra

Five basic types of the ZnO, denote as ZnO-1, ZnO-2, ZnO-3, ZnO-4, ZnO-5 were investigated. They were deposited in the processes which were characterised by the following parameters (Table II).

The diffraction spectra for three different ZnO layers deposited on the standard Corning 0211 ground are presented in Fig. 2. The spectra were obtained by means of Roentgen Cu lamp with the range of the diffraction angles of 2Θ 30–40° (constant $K_{\alpha 1} = 0.154051$ nm).

The data for the crystalline ZnO lattice in the hexagonal configuration: Ao = 0.3249 nm, Co = 0.5205 nm, $2\Theta = 34.438°$ for $\langle 002 \rangle$ direction, $2\Theta = 31.749°$ for $\langle 100 \rangle$ direction, $2\Theta = 36.250°$ for $\langle 101 \rangle$ direction.

The diffraction spectra for the five different ZnO layers, deposited on the silicon ground with aluminium (ground b—chapter 2) and the diffraction spectrum of the ground itself are shown in Fig. 3. The strongest texture is observed for the ZnO-1 lager (according to the data for the ZnO crystalline lattice of the hexagonal arrangement the strongest orientation in $\langle 002 \rangle$ direction was observed). The influence of the aluminium layer (deposited by means of the magnetron sputtering method) on the silicon ground on the spectrum characteristic is also presented in the Fig. 3.

TABLE II The conditions for the ZnO deposition by the magnetron sputtering method

ZnO	P (W/cm^2)	h (μm)	t_1 (h)	T_1 (°C)	p_1 (Pa)	t_2 (h)	T_2 (°C)	p_2 (Pa)	
ZnO-1[a]	2.4	2.7	1.5	200	5	5	320	0.02	50% O_2, 50% Ar
ZnO-2[b]	3.2	1.1	1	200	5	—	—	—	50% O_2, 50% Ar
ZnO-3[b]	3.2	0.8	0.75	200	5	—	—	—	50% O_2, 50% Ar
ZnO-4[b]	2.4	0.9	1.3	200	5	—	—	—	100% O_2,
ZnO-5[b]	3	1.4	0.75	200	5	6	320	0.02	50% O_2, 50% Ar

[a]dc magnetron sputtering.
[b]pulse dc magnetron sputtering.

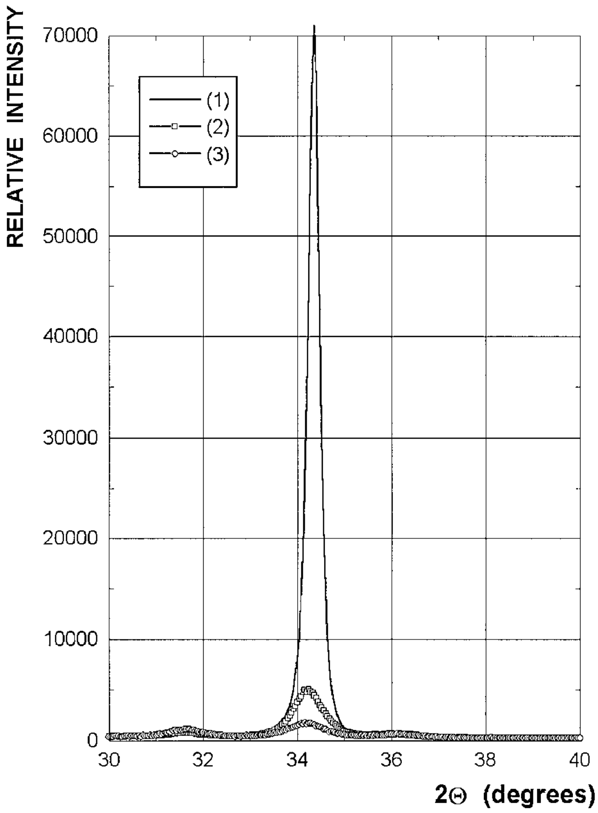

Figure 2 X-ray diffraction patterns for three different ZnO layers on the standard (Corning 0211) ground. (1) ZnO-1 layer, (2) ZnO-3 layer, (3) ZnO-4 layer.

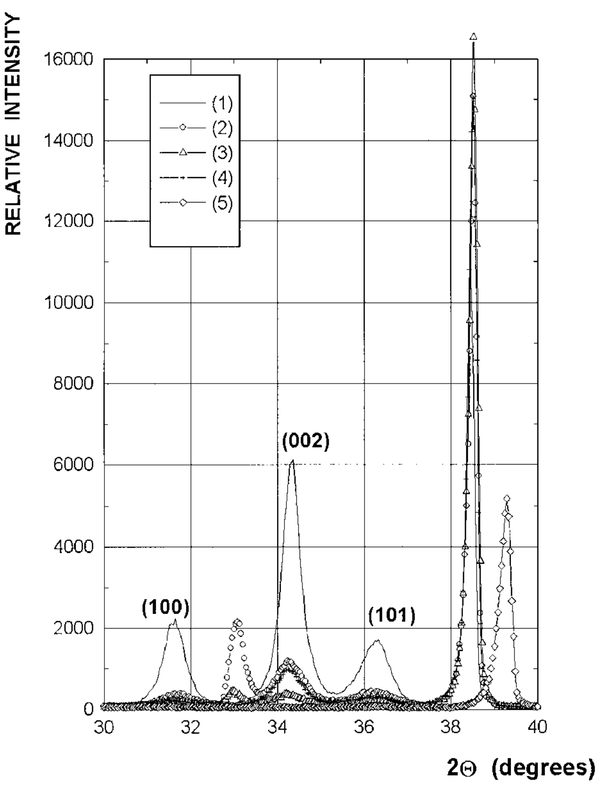

Figure 3 X-ray diffraction patterns of ZnO for four different layers: (1) ZnO-1, (2) ZnO-2, (3) ZnO-3, (4) ZnO-4 on the silicon base with the aluminium film (base "b") and for the ground itself (5).

The comparison of the ground influence on the ZnO layer texture is shown in Fig. 4. Much better piezoelectric parameters (stronger orientation of the *c*-axis in the normal direction were obtained for the glass base).

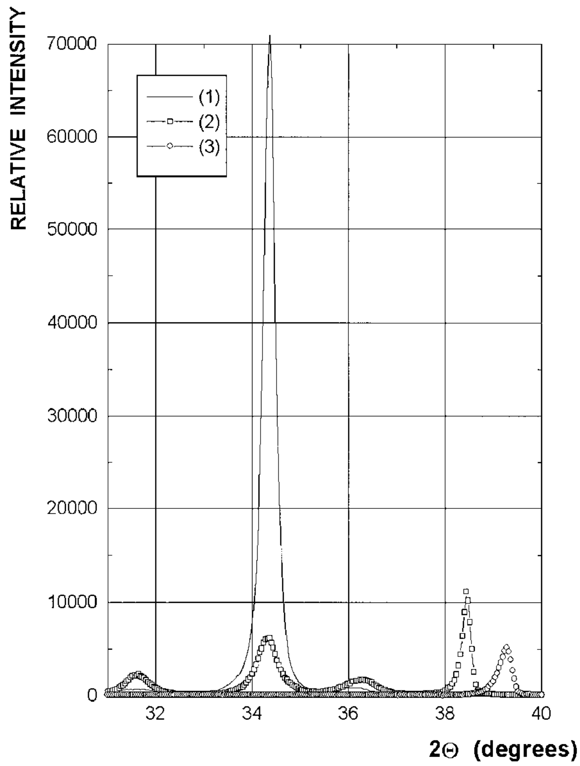

Figure 4 X-ray diffraction patterns for the ZnO-1 layer on the glass Corning 0211 (1), on the "b" ground (Si + Al) (2) and the spectrum of the ground "b" itself (3).

The ground made of crystalline ⟨100⟩ silicon covered with the aluminium layer makes the condition of crystalline ZnO lattice formation worse. The base made of the amorphous glass allows to obtain better texture of the layer in ⟨002⟩ direction. For ZnO-1 layer the thickness of the layer was the greatest and in this case the process of warming was carried out (Fig. 2). The ZnO-3 layer had about three times smaller thickness and in this case there was hot warming. The ZnO-4 layer had weaker texture (Fig. 2) in comparison with the ZnO-3 layer. It could be the result of the applied gas mixture composition. Increasing of the layer thickness as well as using the warming process make the film orientation and the piezoelectric parameters of the layer better. The change of the feed work mode from dc to pulse dc had not any noticeable importance. For the future investigations the ZnO-1 layer was chosen. During the process of its deposition the power density was increased (25%) the time of warming was longer (20%) and the temperature of the ground was higher (10%). This layer was denoted as ZnO-5.

The diffraction spectra of the ZnO-5 layer deposited on three different grounds: (1) silicon/silicon oxide ("e"-ground chapter 2), (2) silicon/chromium ("d"-ground chapter 2), (3) silicon/silicon nitride ("c"-ground chapter 2) are presented in Fig. 5. The chromium layer was deposited on the silicon film by means of the magnetron sputtering method. The best texture was obtained for the ZnO-5 layer on the silicon/silicon oxide ground, that is followed by the ZnO-5 layer on the silicon/silicon nitride ground.

The resistivity of the ZnO layers on the glass ground were equal to the following values (Table III).

In the applications in which the piezoelectric properties of the layers are substantial for ZnO existing in

TABLE III The resistivity of the ZnO layers on the glass ground

ZnO	ZnO-1	ZnO-2	ZnO-3	ZnO-4	ZnO-5
ρ (Ωm)	(1-10)10^8	(2-10)10^{11}	(8-20)10^{11}	(2-10)10^{11}	(4-10)10^8

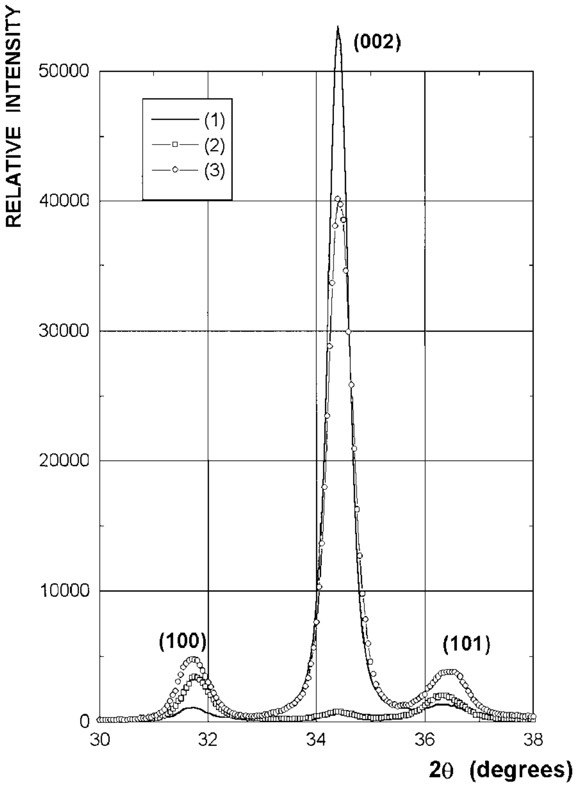

Figure 5 X-ray diffraction patterns for the ZnO-5 layer on the "e" ground (BSG) (1), on the "d" ground (Si + Cr) (2) and on the "c" ground ($Si + Si_3N_4$) (3).

the polycrystalline form it is important for its *c*-axis to be normal to the ground surface. In the hexagonal crystalline lattice it corresponds with ⟨002⟩ direction and such texture shows the best piezoelectric parameters (high electromechanical coupling).

4. Conclusions

Many ZnO samples were produced and investigated under the different technological conditions. They were deposited on the different grounds. The most interesting diffraction spectra for the different samples are presented in Figs 2–5. Basing on the results of these investigations the following conclusions were found out:

1. The texture of the ZnO layer gets better when the thickness of the layer (in ⟨002⟩) direction increases,
2. The texture of the ZnO layer increases after applying the warming process,
3. The influence of the metallic layers, aluminium, chromium is noticeable. These layers make the ZnO texture worse.
4. For the Zn target applied the better parameters were obtained for the gas mixture composition: 50% O_2 + 50% Ar,
5. The introducing of the amorphous ground (i.e., glass, BSG, silicon nitride) considerably increases the ZnO texture,
6. The best parameters were obtained for the ZnO-1 and ZnO-5 layers,
7. The influence of the magnetron work, dc or dc pulse (kHz) has less importance.

The choice of the proper technology is depended on the material of the sensor membrane. For membranes made of the crystalline silicon one should use the buffer layer from the silicon nitrides (about 0.1 μm). There is no need to introduce the additional layers for membranes made of the silicon oxide with boron (BSG). Also the membranes made of silicon nitride can be direct ground for zinc oxide. The application of the metallic layers need the deposition of the buffer film i.e., silicon oxide or silicon nitride layers.

Acknowledgements

The work was sponsored by the Polish State Committee for Scientific Research within grant 8T10C02216 and grant 8T10C02216.

References

1. J. GOLĘBIOWSKI, *Elektronizacja* **9** (1997) 17.
2. *Idem., Proceedings SPIE Optoelectronic and Electronic Sensors* **2634** (1995) 191.
3. K. UOZUMI, K. OHSONE and R. M. WHITE, *Appl. Phys. Lett.* **43** (1983) 917.
4. L. P. SOLIE, *J. Appl. Phys.* **44** (1973) 619.
5. E . A. IRENE, *J. Electronic Mater.* **5** (1976) 287.
6. F. S. HICKERNELL, *J. Appl. Phys.* **44** (1973) 1061.
7. O. YAMAZAKI, T. MITSUYU and K. WASA, *IEEE Trans. Sonic Ultrason.* **27** (1980) 369.
8. J. GOREE and T. E. SHERIDAN, *Appl. Phys. Lett.* **59** (1991) 9.
9. D. F. L. JENKIS, M. J. CUNNINGHAM, G. VELU and D. REMIENS, *Sensors and Actuators* **A63** (1997) 135.
10. T. SAEED and P. O'BRIEN, *Thin Solid Films* **271** (1995) 35.
11. S. S. SCHWARTZ, S. J. MARTIN, S. DATTA and R. L. GUNSHOR, *IEEE Trans. on Ultrason., Ferrelectr. and Freq. Control* **36** (1989) 150.
12. Y. MANABE and T. MITSUYU, *Jpn. J. Appl. Phys.* **29** (1990) 334.

Received 11 November 1998
and accepted 8 April 1999