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Deposition and Optimization of Piezoelectric ZnO-layer using Sol-gel Technique for MEMS Acoustic Sensor

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Abstract

In this paper, ZnO-layer is deposited and optimized using sol-gel technique for piezoelectricity. The optimized piezoelectric ZnO layer is useful in the development of MEMS Acoustic Sensor and similar applications. In ZnO layer deposition, a solution was prepared using precursor [Zinc Acetate Dihydrate (ZAD)] and binder [Monoethanolamine (MEA)] with different solvents [ethanol and n-propanl]. The deposited samples were annealed at 600° C to obtain the piezoelectricity of the layer. The technological development is supported by characterization of samples using Dektak 6M surface profiler and XRD studies of ZnO film. This paper discusses the effects of solvents and substrate materials with respect to the thickness and crystal structure of deposited piezoelectric ZnO film.

Keywords: Piezoelectricity; thin film; ZnO; sol-gel; spin coating; MEMS; Acoustic Sensor;

1. Introduction

ZnO is one of the widely recognized II-VI compound semiconductor materials having direct bandgap of 3.37 eV and a large exciton binding energy of 60 MeV at room temperature [1]. ZnO is possesses three types of crystal structure arrangement such as Zinc Sulphate (ZnS), Zinc Blend, and hexagonal closed packed wurtzite [2]. The wurtzite crystal structure is a tetrahedrally arranged material and it's also shows non-centro-symmetry. The lack of center of symmetry, makes ZnO a piezoelectric material. In recent years, ZnO is becoming an alternate option for other piezoelectric materials like PZT, Quartz, BaTiO3, etc [3]. The piezoelectric coefficient of ZnO is not as good as other piezo materials but because of the low dielectric constant and high curie temperature it is most widely used as a piezoelectric material in various applications [3, 4]. The ZnO radiation resistance property makes it suitable for space application [5]. Besides these standout properties, ZnO has many other applications in development of various devices such as transistor [6], gas sensor [7], photocatalytic [8], anti-reflector [9], light emitting diode [10], MEMS-piezoelectric sensor [11, 12], and UV photodetector [13]. ZnO can be deposited by different techniques such as sputtering [14], evaporation method [15], chemical vapor deposition [16], atomic layer deposition [17] and sol-gel [2]. However, these techniques have some advantage and disadvantages. Some of the disadvantage of these techniques are the requirement of highly maintained clean room, costly equipment and slow deposition rate.

The ZnO deposition by sol-gel technique, is an easy and cost-effective method, which is proposed in this paper. The ZnO thin film crystal properties and its morphology depends on the sol-gel parameters like nature of precursor, binder, solvent, pre and post baking temperature, solution stirring time and its temperature and aging time [2, 18, 19]. The molar ratio of the solution also affects the quality of the thin film [18].The thickness and roughness of the thin-film

are affected by spin coating parameters such as coating speed, spinning acceleration and spinning time [2]. In the present approach, the ZnO deposition and its optimization is carried out using sol-gel technique. The various sol-gel parameters are optimized to get a piezoelectric ZnO layer for the development of MEMS acoustic sensor.

2. Experimental

This section of the paper consists of all experimental processes for optimization of ZnO thin film using sol-gel technique. The details of process flow for deposition of ZnO is shown in Fig. 1.

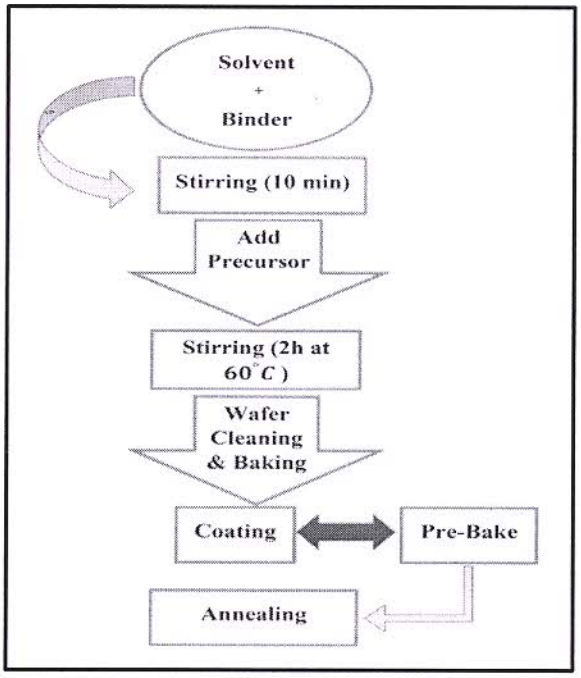


Fig. 1. Flowchart of ZnO deposition using sol-gel technique.

2.1 Materials

There are several types of precursor, binder and solvent are available for ZnO sol-gel synthesis. In this experiment different type of ZnO solution were prepared for the experiment with variation of precursor concentration from 0.2M to 0.6M.
The calculation mass molar solution was carried out using equitation (1) [20].

$$w_s = \frac{(Conc.\ of\ solution) * Molar\ mass\ of\ chemical * Taken\ Solvent\ (ml)}{1000\ ml} \quad (1)$$

Where, w_s is the amount of chemical in gram.

For this experiment, absolute ethanol [(C_2H_5OH), chemical purity 99.95%] (Et-OH) and n-propanol [(C_3H_8O) chemical purity 99.95%] were used as solvents. Zinc acetate dehydrate [(Zn $(CH_3COO)_2)_2.2H_2O$, chemical purity 99.95%] (ZAD) and monoethanolamine [$(HOC_2H_4).NH_2$, chemical purity 99.5%] (MEA) were taken as precursor and binder respectively.

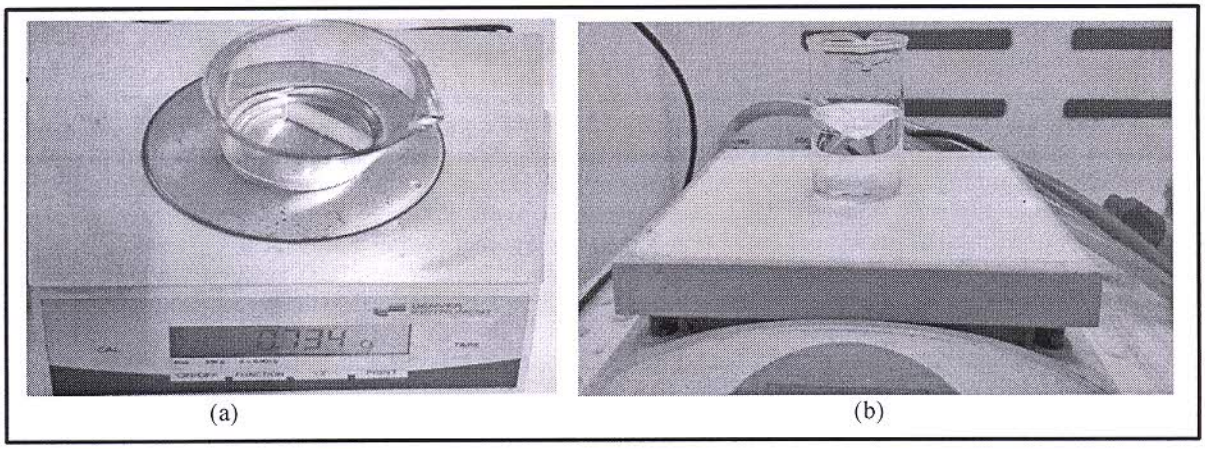
2.2 Solution Preparation

First of all, the appropriate amount of solvent with binder (MEA) was taken and stir for 10 min at $60^{\circ}C$ temperature. Then after, ZAD was added into the homogeneous solution and kept stirring for the next 2 hour at

60° C in an open environment with the help of the hot-plate. After stirring, clear and homogenous ZnO solution was obtained. The prepared ZnO solution was kept for aging. The solution aging is necessary for ZnO nucleation growth and also it help to increase the viscosity. The chemical amount was calculated by equation 1.The details of solution preparation is given Table 1.

Table 1. The details of solution preparation

S. No.	Solution type	Conc. of ZnO Solution	Solvent		Amount of ZAD	Amount of MEA	Stirring Temp.	Stirring Time
			Name	Amount			Temp.° C	
1	Sol. (A)	0.2	Ethanol	30 ml	1.32 g	0.366 g	60° C	2 hours
2	Sol. (B)	0.4	Ethanol	30 ml	2.63 g	0.733 g	60° C	2 hours
3	Sol. (C)	0.6	Ethanol	30 ml	3.95 g	1.99 g	60° C	2 hours
4	Sol. (D)	0.4	N-propanol	30 ml	2.63 g	0.733 g	60° C	2 hours



(a) (b)

Fig. 2. Experimental Setup: (a) Weighing of chemical and (b) Solution Stirring.

2.3 Solution Coating

P-type (100) silicon wafers were taken as a base substrate and then silicon oxide layer was grown and deposited via thermal oxidation and PECVD respectively. After oxide growth and deposition these wafers were cleaned properly using standard piranha cleaning process. After then wafers were kept for moisture bake for 30 min at 150° C in an oven.

After substrate preparation, ZnO solution was coated on the wafer with the help of spin coater. Spin coating parameters like spinning speed, acceleration and spinning time are affected the thickness and uniformity of the film. The necessary coating parameters which affects the film quality are given in Table 2. It was observed that the film thickness increases with number of coating.

Table 2. Details of deposition parameters

S. No.	Sample Type	Substrate $Si + SiO_2$	Type of Used Solution	Coating parameter		Prebaking Temp.	Annealing Temp.	No. of Coating
				Speed	Time	Temp.° C	Temp.° C	
1	S-1	PECVD	Sol. (A)	4000	30 sec	180° C	600° C	8 times
2	S-2	PECVD	Sol. (B)	4000	30 sec	180° C	600° C	8 times
3	S-3	PECVD	Sol. (C)	4000	30 sec	180° C	600° C	8 times
4	S-4	PECVD	Sol. (D)	4000	30 sec	180° C	600° C	8 times
5	T-1	PECVD	Sol. (B)	4000	30 sec	170° C	600° C	10 times
6	T-2	THERMAL	Sol. (B)	4000	30 sec	170° C	600° C	10 times

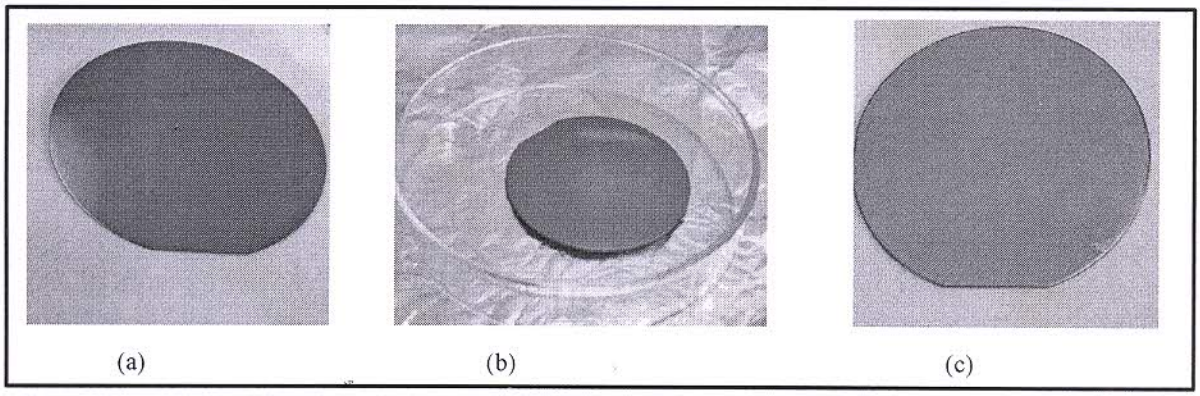


Fig. 3. Deposition of ZnO Layer: (a) wafer without ZnO Coating, (b) Pre-baking of film and (c) Annealed Sample after $600^{\circ}C$

3. Result and discussion.

3.1 Thickness Measurement.

The thickness of deposited ZnO layer was carried out by creating a step height using photolithography technique as shown in Fig. 4. In the process, a positive photoresist S1818 was used. After patterning, ZnO was removed from unwanted area using HCl solution. Finally, the thickness of deposited ZnO layer was measured using Dektak 6M surface profiler and shown in Fig. 5. Fig 5(a) and 5(b) shows the thickness measurement of two different samples having different solution concentration with same number of coating. In Fig. 5(a), the solution concentration was taken 0.4 mole whereas in Fig. 5(b) the solution concentration was 0.2 mole. It has been observed from Fig. 5 that the higher concentration gives higher thickness with same number of coating. In this way, by optimizing the spin coating parameters we can get a desired thickness of ZnO layer which is required for the development of MEMS acoustic sensor.

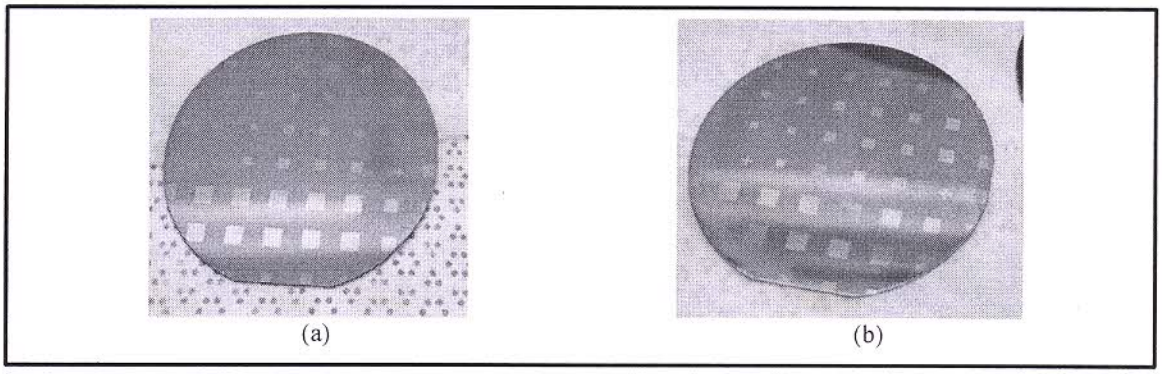


Fig. 4. Pattern of ZnO thin film: (a) 0.4M solution deposited film and (b) 0.2M solution deposited film

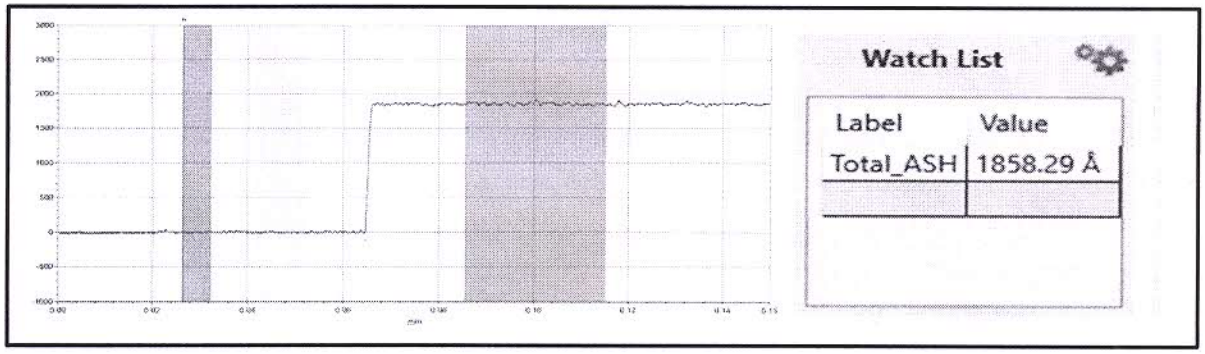


Fig. 5. (a) Thickness measurement of 0.4M solution deposited sample.

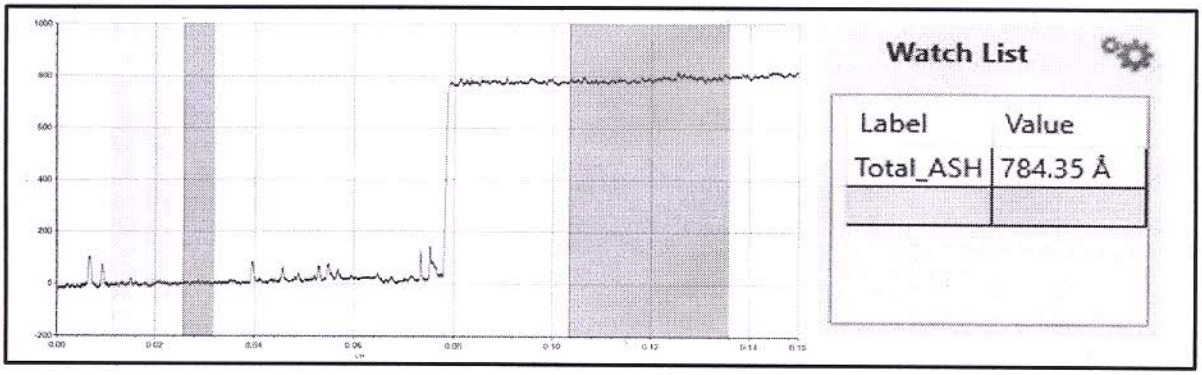


Fig. 5. (b) Thickness measurement of 0.2 M solution deposited sample

3.2 XRD Characterization

The crystal structure and crystallographic orientation of sol-gel deposited thin film has been characterized by X-ray diffractometer. For this characterization, Cu used as a X-ray source with Kα value 0.154 nm. The crystal size of the film depends on width of the peak and is calculated by Debye-Scherrer equation (2) [21].

$$D = \frac{K*\lambda}{\beta*Cos(\theta)} \tag{2}$$

where, K is Scherrer constant (0.94), λ is wavelength of X-Ray (0.154 nm), β is FWHM (Full Width Half Maxima) and D is crystallite size

The XRD characterization results of different samples are shown in Fig. (6). The XRD results suggest that crystallographic orientation of thin film depends on the sol gel parameters. The standard data file, JCPDS 36-1451 confirms that all deposited thin films are crystalline with hexagonal crystal structure. Fig. 6 (a) shows that the preferential growth of the film depends on the substrate materials. It is observed from this Fig. that the ZnO deposited on PECVD substrate gives better result. The (002) peak is more dominating in nature on PECVD SiO_2 in comparison to ZnO deposited on thermally grown oxide layer. Crystallite size of ZnO deposited on PECVD substrate and thermally grown SiO2 substrate are found to be 22.19 nm and 21.87 nm respectively. It is also clear from calculation that the crystallite size of ZnO for both substrates are very close to each other. However, ZnO deposited on PECVD layer has better piezoelectric properties in comparison ZnO deposited on thermally grown oxide layer.

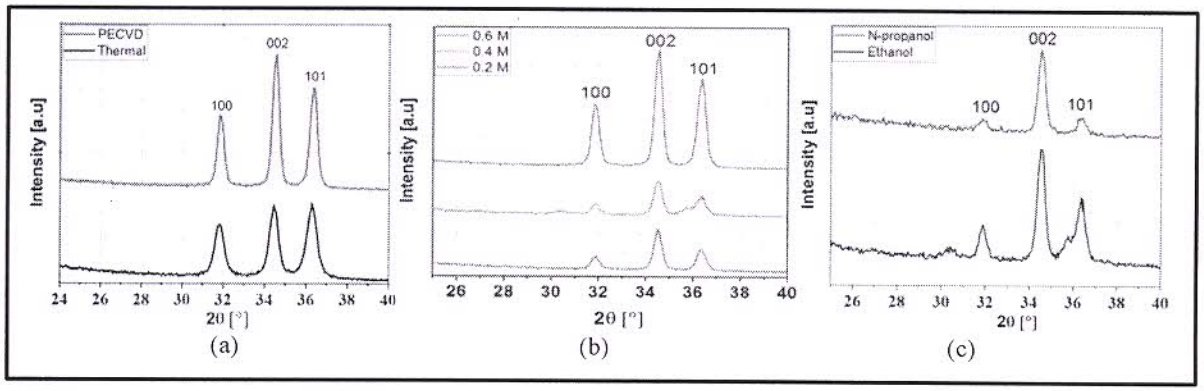


Fig. 6 XRD pattern: (a) T-1 & T-2 Sample, (b) S-1, S-2 & S-3 sample and (c) S-2 & S-4 sample

XRD pattern of Fig. 6. (b) shows that the 0.2 M graph gives better result compare to another molar solution of the film. So, it can be deduced that Conc. Also, play a critical role in the sol-gel deposition of ZnO. Preferred orientation (single crystal) decreases when conc. of Zn increases. It is clear that the lower Zn Conc. solution gives better oriented (002) film, but it also gives lower thickness after the same No. of the coating. For the acoustic devices, the thickness of piezoelectric layer is also important therefore, we need to fix the spin coating parameters and solution concentration for optimum sensitivity of acoustic sensor.

Fig. 6. (c) is shows that the n-propanol based solution gives better quality film (highly oriented along c-axis) in comparison to ethanol-based solution. Due to higher boiling point of n-propanol ($98^{\circ}C$), evaporation of solution less and gives better (002) peak. Whereas, lower boiling temperature of ethanol ($78^{\circ}C$) gives faster evaporation and finally less (002) oriented film.

Table 3. XRD results of different samples

S. No.	Sample Name	Conc. (ZAD)	FWHM	Crystal Plane	2θ	Crystallite size
1	S-1	0.2	0.404	002	34.52	21.55 nm
2	S-2	0.4	0.407	002	34.52	21.37 nm
3	S-3	0.6	0.393	002	34.52	22.19 nm

The value of 2θ for (002) peak from the standard JCPDS files is 34.42 but for the deposited film the value of (002) is slightly bigger because of compressive stress between thin film and substrate. This type of stress generated due to lattice mismatch between thin film and substrate.

4. Conclusion

ZnO film has been deposited and optimized using sol-gel technique for MEMS acoustic sensor and similar applications. It is concluded that the piezoelectricity of the film depends on solution concentration, substrate material, solvent and spin coating parameters. The XRD results confirm that 002 oriented hexagonal wurtzite ZnO thin film was successfully deposited by so-gel technique using n-propanol as a solvent. The effect of substrate on quality of the film studied and better crystalline growth of ZnO film along the c-axis was found on the PECVD substrate. The XRD results of sample deposited by 0.2M solution concentration shows high intensity of 002 peak compare to 0.4M and 0.6M solution concentration. The variation of ZnO deposited thin film with solution concentration gives the idea to achieve the desired thickness of piezoelectric layer for MEMS acoustic sensor.

5. Acknowledgment

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