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Growing parameters and quality of ZnO seed-layer film. Part 2

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The results of deposition of ZnO seed-layer on the silicon substrate, Al-coated silicon and Al-coated lithium niobate substrates by sol-gel method at sol concentration of 0,8 and 1,2 M were introduced. It was shown that film roughness and grain size had increased with increasing of the sol concentration. The new results of synthesis of ZnO vertically oriented nanorods on the obtained thin seed-layer on the silicon substrate by hydrothermal method were presented. The diameter and density of synthesized ZnO nanorods were defined, the dependence between such geometrical parameters and seed-layer properties was shown. The obtained results could be applied for design of acoustic wave sensors and nanoscale devices. References 5, figures 5.

Keywords: *ZnO seed-layer, ZnO nanorods, sol-gel, sol concentration, hydrothermal method. Introduction.*

Introduction

Investigation of novel materials for nanoscale devices is an actual problem for the present science and technology. ZnO is attracting considerable attention due to its unique ability to form a variety of nanostructures such as nanorods, nanowires, nanoribbons/nanobels, nanocombs, nanorings, nanocages, nanocastle, nanofibers etc. ZnO nanorods/nanowires have been employed as bio- or gas sensitive element of acoustic wave sensors [4]. Hydrothermal method for synthesis of ZnO nanostructures has many advantages when compared to the most common vapor-phase synthesis, such as low-cost, low temperature, scalability and ease handling [1].

In the first part of our article [2] we made critical review of the effects of different growing conditions on the structure and properties of obtained by sol-gel method ZnO seed-layer film for ZnO vertically oriented nanorods growth. Almost any substrate can be used for the growth of ZnO vertically oriented nanorods by using ZnO seed-layer film, but deposition on the Al film by sol-gel method have not been completely studied. The sol concentration is the most important parameter of growth process of ZnO seed-layer film for obtaining of high-quality ZnO nanorods.

In this part we presented the new obtained results of preparation of the ZnO seed-layer on Al-coated silicon substrate, Al-coated lithium niobate substrate and silicon substrate by sol-gel growth method with the sol concentrations of 0,8 and 1,2 M. We reported about growing of ZnO nanorods on silicon substrates with as-prepared different seed-textured ZnO thin layers. The results could be useful for manufacturing of novel acoustic wave sensors, photoelectric transducer and nanoscale devices.

Experimental details

There were two main steps in ZnO nanostructures growing: (1) preparation of a ZnO seed-layer by sol-gel method and (2) the nanostructures array growth by hydrothermal method. We carried out two stages of study. The first stage consisted of a ZnO thin seed-layer preparation on Al-coated silicon substrate, Al-coated lithium niobate substrate and silicon substrate by sol-gel growth method. ZnO nanorods were grown on silicon substrates with prepared in the first stage different ZnO seed-layers for the second stage of the study. We used similar to [5] technic but with some improvement which are described.

Initially the substrates were cleaned with hydrogen peroxide H_2O_2 at 30°C for 30 min. For the first step zinc acetate dihydrate (ZnAc) $Zn(COOCH_3)_2 \cdot 2H_2O$ was used as the starting salt material to prepare ZnO thin films by sol-gel method. The zinc acetate dihydrate was dissolved in isopropanol $((CH_3)_2CHOH)$. Then monoethanolamine (MEA) $HOCH_2CH_2NH_2$ solution was added at room temperature. The concentration of zinc acetate was 0,8 and 1,2 mol/l and molar ratio of MEA to ZnAc was kept to 1,0. The mixture was stirred by a magnetic agitator at 65°C until a clear and homogeneous solution formed. Prepared sol-gel was cooled to room temperature and filtered with 0,22 μm membrane filter. Film deposition was carried out in air at room temperature. The precursor solution was spin coated at 3000 rpm for 30 s on the substrates. After each coating the coated film was dried at 100°C for 30 min at the sintering furnace. The preheat-treatment temperature at 100°C is required for the complete evaporation of organics and the initiation of formation and crystallization of the ZnO film [3]. After the deposition of the fifth layer, the resulting thin films were annealed at 400°C, in air for 1 h to obtain the homogeneous and stable film.

For the second step ZnO nanorods growth was carried out at 65°C under stirring with a magnetic agitator for 90 min on silicon substrates with prepared in the first stage of the experiment different ZnO seed-layers. The solution consisted of analytically pure zinc nitrate hydrate $Zn(NO_3)_2 \cdot 6H_2O$ and analytically pure hexamethylenetetramine $C_6H_{12}N_4$ which were mixed with an equal molar concentration. The chemicals were solved in deionized water, resulting in a transparent solution. The concentration of both zinc nitrate and HMT was 0,025 mol/l. At a temperature of about 65°C the solution starts to become cloudy, indicating that the chemical reactions have started. During the growth process the solution was stirred in order to obtain a homogeneous concentration and temperature throughout the reactor volume. After the reaction the samples are thoroughly purged with deionized water and dried at room temperature.

Scanning electron microscopy (JEOL Ltd., NeoScope JCM-5000) was used to examine the morphology of seed-layers and especially the diameters of the ZnO nanorods.

Results and discussion

The ZnO seed-layers were deposited on the on the Al-coated silicon substrate, Al-coated lithium niobate substrate and silicon substrate using the sol-gel method with sol concentrations of 0,8 and 1,2 M. Scanning electron microscopy images of the layers on such substrates are presented on Fig.1, 2, 3 respectively.

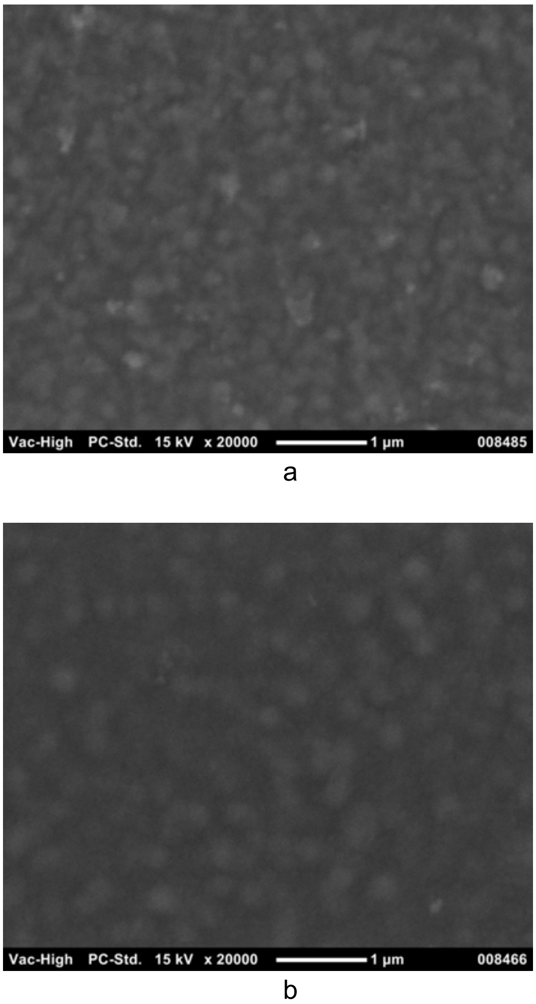
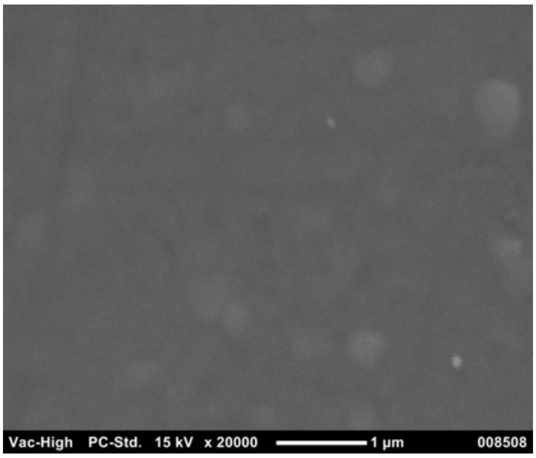
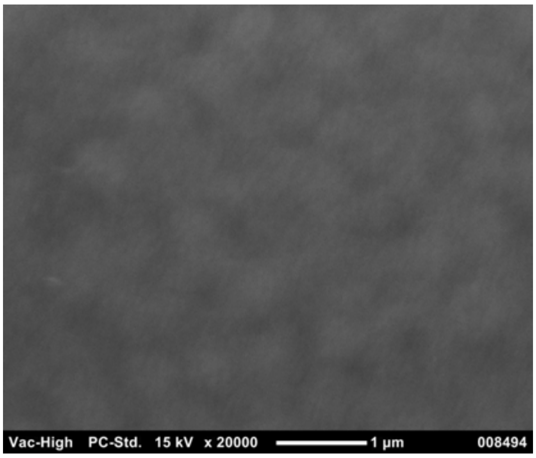


Fig. 1. SEM images of seed-layers deposited on the Al-coated silicon substrate (a – the sol concentrations was 0,8 M and b – the sol concentrations was 1,2 M)

The SEM images for all types of substrates showed strong dependence between a sol concentration and characteristics of seed-layer. At the sol concentration of 0,8 M smooth layers with small ZnO seeds and regular structure were obtained. The seed-layers looked like a homogenous film. The roughness of seed-textured layers increased with increasing of the sol concentration. At the sol concentration of 1,2 M seeds had apparent contours and diameter 50-90 nm. In addition periodicity property and uniformity were better for uncoated Si substrate.

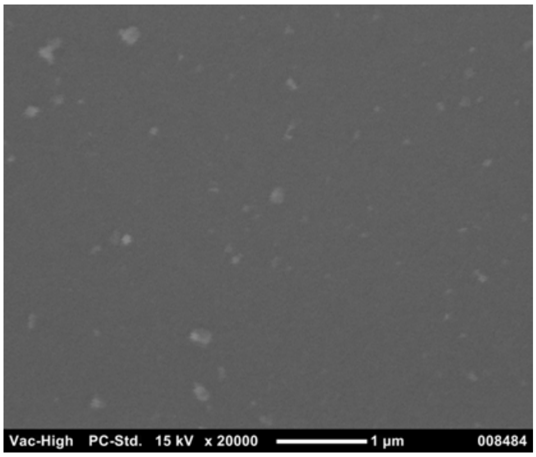


a



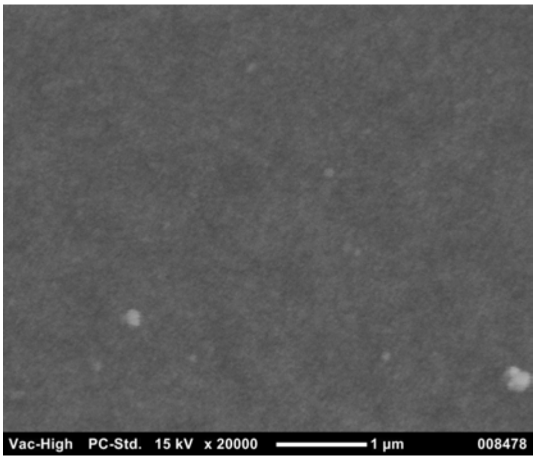
b

Fig. 2. SEM images of seed-layers deposited on the Al-coated lithium niobate substrate (a – the sol concentrations was 0,8 M and b – the sol concentrations was 1,2 M)



a

A



b

Fig. 3. SEM images of seed-layers deposited on silicon substrate (a – the sol concentrations was 0,8 M and b – the sol concentrations was 1,2 M)

The ZnO nanorods were grown on silicon substrates with prepared ZnO thin seed-layers (Fig. 3) using sol concentrations of 0,8 and 1,2 M. Scanning electron microscopy images are presented on Fig.4 and 5.

It was shown significant influence of sol concentration on the grain size of the ZnO thin seed-layer. Parameters of seed-textured ZnO thin layer affected the shape (alignment, length, diameter, etc.) of the ZnO nanorods. The SEM images showed that the alignment of the nanowires grown on the ZnO film prepared with sol concentration of 1,2 M is significantly better than those prepared on the film with the sol concentration of 0,8 M. The diameter of the nanorods are 35±10 nm and 62±5 nm respectively for films prepared with sol concentration of 0,8 M and 1,2 M. The density of the ZnO nanorods were 76·108 cm-2 and 100·108 cm-2 for films prepared with sol concentration of 0,8 M and 1,2 M.

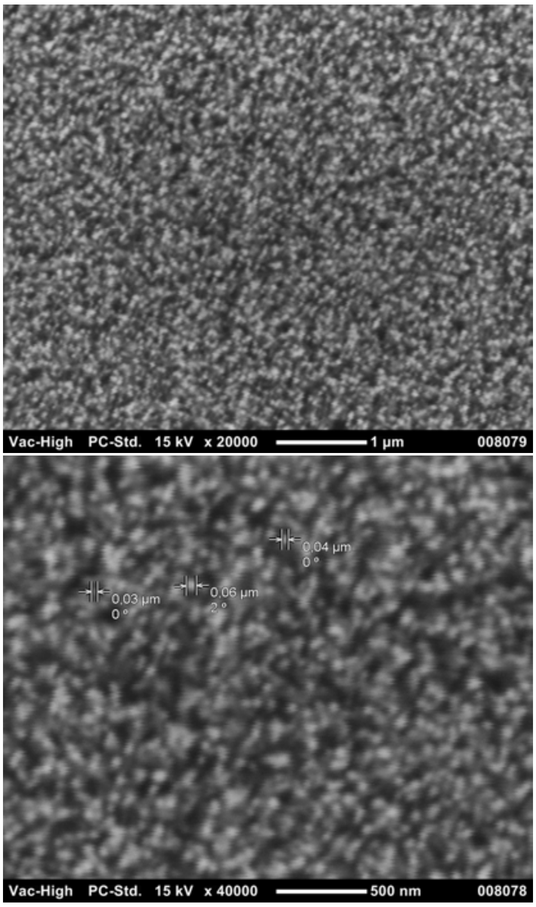


Fig. 4. SEM images of ZnO nanorods synthesized on a Si substrate coated with ZnO thin seed-layer using sol concentrations of 0,8 M

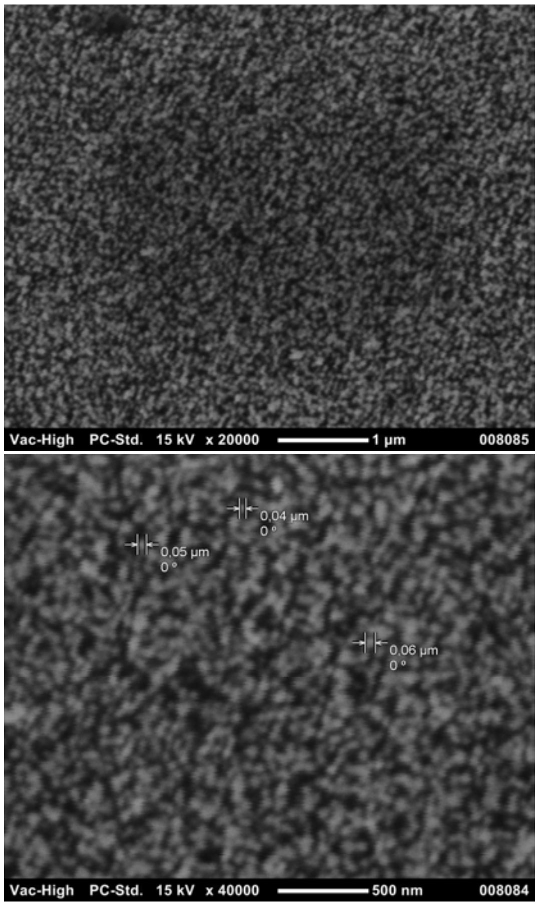


Рис. 5. SEM images of ZnO nanorods synthesized on a Si substrate coated with ZnO thin seed-layer using sol concentrations of 1,2 M

Conclusion

In this paper new results of preparation of the seed-textured ZnO thin layer on Al-coated silicon substrate, Al-coated lithium niobate substrate and silicon substrate by sol-gel growth method with sol concentrations of 0,8 and 1,2 M we presented. It was shown the significant influence of sol concentration on the properties of seed-textured ZnO thin layer and the shape of the ZnO nanorods. The roughness, grain size of the ZnO films increased with the increase of the sol concentration.

ZnO nanorods on silicon substrates with as-prepared different seed-textured ZnO thin layers were synthesized by hydrothermal method. ZnO nanorods grown on substrate with higher sol concentration for the ZnO thin seed-layer were more vertical and had higher density. Obtained results could be applied in manufacturing of novel acoustic wave sensors and other devices for nanoelectronics.

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References

1. *Bai Shr-Nan*, Synthesis of ZnO nanowires by the hydrothermal method,using sol–gel prepared ZnO seed films / Shr-Nan Bai, Shich-Chuan Wu // J Mater Sci: Mater Electron. – 2011. – 22. – P. 339–344.
2. *Bogdan A., Orlov A., Ulianova V.*, Growing parameters and quality of ZnO seed-layer film (Part 1) / A. Bogdan, A. Orlov, V. Ulianova // Electronics and Communications. –2012. – №6.

3. *Ilican S.,* Preparation and characterization of ZnO thin filmsdeposited by sol-gel spin coating method / S. Ilican, Y. Caglar, M. Caglar // Journal of optoelectronics and advanced materials. – 2008. – Vol. 10, No. 10. – P. 2578 – 2583.
4. *Lu Yicheng*, Multifunctional Biosensor Based on ZnO Nanostructures / Lu Yicheng // Acoust. Soc. Am. – 2012. – Vol. 131, Issue 2, – P. 1667-1667.
5. *Raoufi D., Raoufi T.,* The effect of heat treatment on the physical properties of sol-gel derived ZnO thin films / Davood Raoufi, Taha Raoufi // Applied surface science. – 2009. – Vol. 225. – P. 5812-5817.

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Параметри росту та якість плівки зародкового шару ZnO. Частина 2

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Представлено результати отримання зародкового шару ZnO за допомогою золь-гель методу при концентраціях золю 0,8 та 1,2 М на підкладках кремнію, на підкладках кремнію та ніоботу літію з плівкою алюмінію. Показано, що зі збільшенням концентрації золю шорсткість плівки та діаметр зерна збільшуються. Подано результати синтезу вертикальних стрижневих структур ZnO на отриманих тонких плівках зародкового шару за допомогою методу гідротермального синтезу на підкладках кремнію. Визначено діаметр і густину синтезованих стрижневих структур ZnO, показано залежність таких геометричних параметрів стрижневих структур від властивостей зародкового шару. Отримані результати можуть бути використані для створення сенсорів на акустичних хвилях та нанорозмірних приладів. Бібл. 5, рис. 5.

Ключові слова: *зародковий шар ZnO, нанострижні ZnO, золь-гель, концентрація золю, гідротермальний метод.*

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Параметры роста и качество пленки зародышевого слоя ZnO. Часть 2

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Представлены результаты получения зародышевого слоя ZnO с помощью золь-гель метода при концентрациях золя 0,8 и 1,2 М на подложках кремния, на подложках кремния и

ниобата лития с пленой алюминия. Показано, что с увеличением концентрации золя шероховатость пленки и диаметр зерна увеличиваются. Приведены результаты синтеза вертикальных стержневых структур ZnO на полученных тонких пленках зародышевого слоя с помощью метода гидротермального синтеза на подложках кремния. Определены диаметр и плотность синтезированных стержневых структур ZnO, показана зависимость таких геометрических параметров стержневых структур от свойств зародышевого слоя. Полученные результаты могут быть использованы для создания сенсоров на акустических волнах и наноразмерных приборов. Библ. 5, рис. 5.

Ключевые слова: *зародышевый слой ZnO, золь-гель, наностержни ZnO, концентрация золя, гидротермальный метод.*

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