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ZnO Growth on Macroporous Si Substrates by HF Magnetron Sputtering

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It is the purpose of this work to research the formation process of zinc oxide by the method of HF magnetron sputtering on silicon substrates of orientation (100) with the previously applied system of macropores. Samples of porous silicon were obtained by electrochemical etching. *n*-type Si (100) wafers were used. Precipitation of thin ZnO films was carried out in an RF discharge in an argon atmosphere with oxygen by sputtering a zinc target. The target had a diameter of 80 mm and a thickness of 6 mm. The deposition time was 1200 s. The pressure in the growth chamber was maintained at a level of 10^{-3} Pa. The substrate temperature was fixed at 300 °C. X-ray examination of ZnO has shown that the films have a polycrystalline nature with a wurtzite-type structure and hexagonal phase. ZnO crystallites in the coatings are highly oriented along the *c*-axis and perpendicular to the substrate surface. The lattice constant along the crystallographic *c*-axis of ZnO film was 5.2260 Å. The average crystallite size calculated by the Selyakov-Scherrer formula was 12 nm. According to SEM, grain size was ~ 50-100 nm. These discrepancies are explained by the presence of microstrains in the atomic matrix of the sample, as well as instrumental factors. The microelement analysis revealed practically perfect stoichiometry of ZnO grown on porous-Si/Si.

Keywords: Porous-Si, ZnO films, Method of HF magnetron sputtering.

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1. INTRODUCTION

Transparent conductive oxide coatings, among which zinc oxide is ranked high, are one of the most promising film coatings. The heightened interest is caused by a unique combination of optical and electrophysical properties of zinc oxide. Zinc oxide (ZnO) is widely used in technology, in particular, in photoresponse [1, 2], short-wave semiconductor light emitting diodes [3, 4], thin-film solar cells [5, 6], gas sensors [7], photodetectors [8], memristive devices [9]. At the moment, the question arises of obtaining ZnO films with the given functional characteristics that can find wide industrial applications in devices based on ZnO layers.

ZnO films are obtained by various methods: thermal evaporation, chemical vapor deposition (CVD), spray pyrolysis, etc. Along with the above methods, a special place is occupied by the method of HF magnetron sputtering that has several advantages: good adhesion of the film to the substrate, thickness uniformity and high density of coatings, the possibility of varying electrical and structural properties of an applied coating, controllability and long-term process stability [10]. To obtain ZnO films, gallium nitride (GaN) and silicon carbide (SiC) substrates can be used. However, the cost of these large-diameter substrates is high enough. In order to reduce the cost of the produced heterostructures on the basis of ZnO films, silicon (Si) is often used as a semiconductor substrate.

Attempts have been made recently to obtain films on the porous surface of semiconductors, which is connected with the possibility of optimizing the conditions of grain dimensions, oxygen vacancies, defects, etc. [8, 10-12]. Such heterostructures can be used in the manufacture of LED chips emitting white light (a combination of blue and green emission from ZnO and red and orange emission from porous silicon) [13]. In this regard, a further study of the formation of a porous structure in the ZnO/Si system and its influence on the elastic stresses in the system seems to be relevant. We have already studied the growth mechanisms of silicon carbide (SiC) films by the method of substitution of atoms on macro- and mesoporous silicon substrates (Si) with *p*- and *n*-conductivity types of orientation (100) and (111) [14]. The growth mechanisms of GaN films obtained by the HVPE method (Hydride Vapor Phase Epitaxy) on SiC synthesized by the method of substitution of atoms on mesoporous substrates [14, 15] are investigated.

The aim of this work is to study the process of formation of ZnO by the method of HF magnetron sputtering on silicon substrates of orientation (100) with the previously applied system of macropores.

The paper contains the results and discussion of the research and samples obtained using the following methods: X-ray diffraction measurements and scanning electron microscopy. The X-ray diffraction measurements were made on a MiniFlex 600 installation (Rigaku, Japan) (radiation CuKα1, wavelength $\lambda = 1.5418$ Å). The structure of the surface of phase separation and the surface structure of ZnO layers on porous Si was investigated using a Tescan Mira 3 LMU scanning electron microscope and an energy dispersive spectrometer Oxford Instruments X-Max 80 mm^2.

2. THE METHODOLOGY OF THE EXPERIMENT

The samples of porous silicon were obtained by the method of electrochemical etching using *n*-type Si (100) wafers with a resistivity of 1.0 ÷ 1.5 Ohm·cm. The anodizing process was performed using an electrolyte solution consisting of hydrofluoric (HF) acid and ethanol

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(C_2H_5OH) in a 1:1 ratio. The current density was $J = 31.64$ mA/cm^2. At stage one, SiO_2 film is created on the surface of an n-type silicon wafer, in which a grid of regular openings (windows) is formed by the photolithography method. Then etch pits are created in the windows in the form of inverted pyramids. After that, electrochemical etching is performed with the additional backlighting. The parameters of macroporous silicon samples are shown in Table 1.

Table 1 – Parameters of porous Si (100)

Parameter	Value
Depth of porous layer h, m	150×10^{-6}
Pore diameter d, m	500×10^{-9}
Distance between the pores, m	1.4×10^{-6}
Wafer dimensions, m^2	10^{-4}

The sputtering of ZnO films was performed by HF magnetron sputtering of a zinc target. The substrates were fixed in the device with the help of special clamps that carried out their movement inside the vacuum chamber. The substrate and the target were placed parallel to each other. The parameters of deposition of thin ZnO films by the magnetron sputtering method of a zinc target are shown in Table 2. The vacuum system was pumped out to the level of 10^{-3} Pa just before the obtaining of films.

Table 2 – The deposition parameters of ZnO thin films

Parameter	Value
Residual pressure in the chamber, Pa	10^{-3}
Argon pressure, Pa	1
Oxygen pressure PO_2, Pa	0.1
Substrate temperature, °C	300
Power at the HF magnetron discharge, W	200
Target-substrate distance, m	0.07
Deposition time, s	1200

3. RESULTS AND DISCUSSION

The SEM images of the surface and cleaved facets of ZnO/porous-Si samples (Fig. 1) demonstrate a significant change in the surface morphology after the synthesis. Thus, on the surface of the samples, the structure of small (about tens to one hundred nanometers) crystallites is observed. The sample preserved its original structure in the form of a grid (Fig. 1b).

It can be noticed that the thin ZnO film is closely connected to the porous silicon substrate, and no gap is detected in the interface. This may be due to the partial filling of the pores with the thin ZnO film on the substrate surface (Fig. 1d).

The microelement analysis was performed at two different points of the ZnO film over the surface of the sample (Fig. 3). The content of Zn and O turned out to be 50 % for each element with a statistical error of less than 2 % for point 1 and less than 5 % for point 2 (Fig. 3, Table 3), which is indicative of high stoichiometry of the ZnO film on porous-Si (100).

Furthermore, peaks corresponding to the elements of the substrate can be observed (Fig. 2).

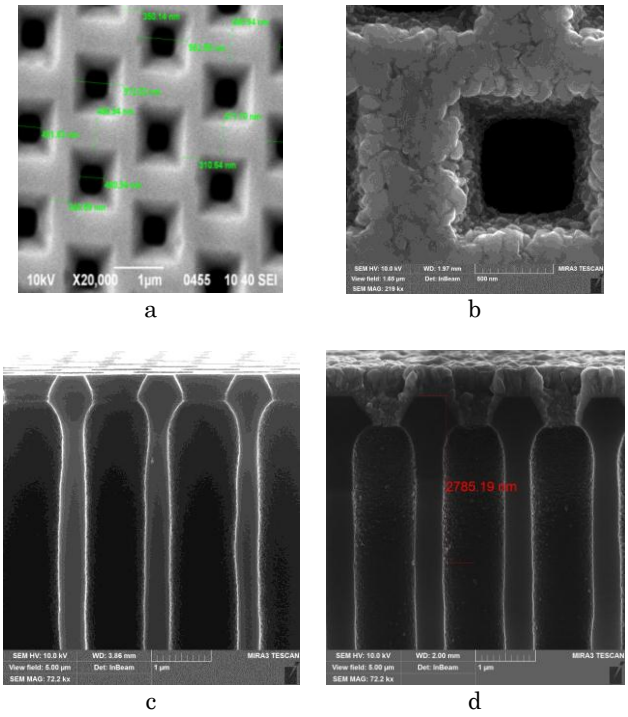

Fig. 1 – The SEM images of the surface (a, b) and cleaved facets (c, d) of the ZnO layer formed on the Si (100) surface with the previously applied system of macropores

The estimated thickness of the ZnO film is about 1-3 μm. The depth of penetration of ZnO nanoparticles into the pores of the substrate is ≈ 2.8 μm (Fig. 1d).

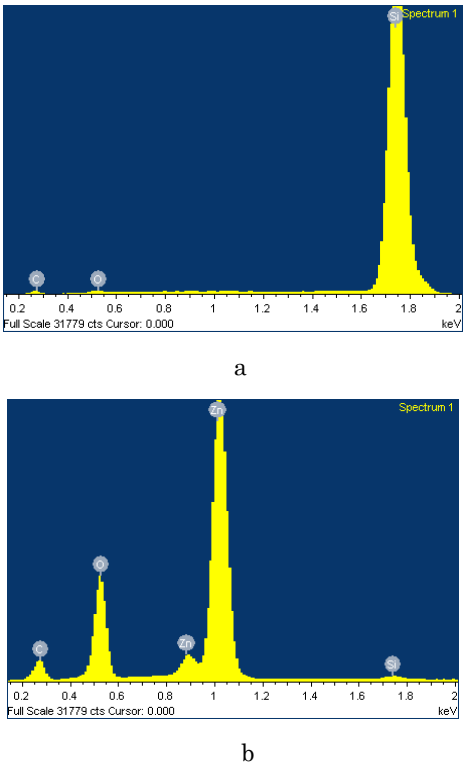

Fig. 2 – The results of the X-ray fluorescent analysis of porous Si (a) and ZnO film on a porous Si (b)

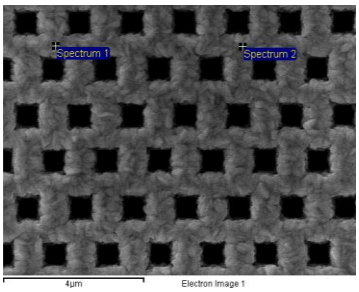

Fig. 3 – The SEM image of the sample (spectrum registration area)

Table 3 – Quantitative analysis using energy dispersive X-ray spectroscopy method

Spectrum	In stats.	O	Si	Zn
Spectrum 1	Yes	48.89	0.92	50.19
Spectrum 2	Yes	45.53	0.49	53.98

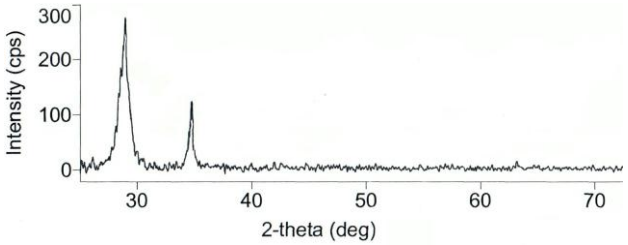

Fig. 4 – X-ray diffraction patterns of ZnO films grown on macroporous Si (001) substrates

Fig. 4 shows the X-ray diffractogram of the ZnO film. An X-ray examination of the crystal structure of ZnO coatings has shown that they have a polycrystalline nature with a wurtzite-type hexagonal lattice. X-ray diffraction pattern has the main diffraction peak (002) that is observed at $2\theta = 34.64°$. The crystallites in ZnO coatings are highly oriented along the *c*-axis and perpendicular to the surface of the substrate. The lattice constant along the crystallographic axis of the ZnO film was 5.2260 Å.

The average dimensions of the crystallites are calculated by the Scherrer formula for X-ray particle size that links the crystallite dimension L in the direction corresponding to this reflection and the width of the reflection at a half-height (FWHM):

$$L = \frac{K\lambda}{W\cos\theta}, \qquad (1)$$

where λ is the wavelength, W is the FWHM of a reflection in radians along 2θ-scale, θ is the angular position of reflection, K is the dimensionless parameter depending on a crystal grain form (as a rule, close to 1).

According to calculations, the average crystallite size was 12 nm, which is slightly smaller than the crystallite size according to the SEM results (Fig. 1b). These discrepancies can be explained by the fact that not only the effect caused by spatial grain dimensions (Selyakov-Scherrer) but also microdeformations in the atomic matrix of a sample as well as instrumental factors contribute to the extension of reflections of the X-ray diffraction analysis. Therefore, the real dimensions of nanoclusters consisting of particle conglomerates can be significantly larger than the values calculated from the estimate of FWHM according to the Selyakov-Scherrer model.

4. CONCLUSIONS

In the present work, the ZnO films on silicon substrate of orientation (100) with previously applied system of macropores were obtained by the method of HF magnetron sputtering. X-ray examination of ZnO has shown that the films have a polycrystalline nature with a wurtzite-type hexagonal phase. The estimated ZnO film thickness is about 1-3 microns. The penetration depth of ZnO nanoparticles into the pores of the substrate is ≈ 2.8 µm. The average crystallite size calculated by the Selyakov-Scherrer formula was 12 nm. According to SEM, grain size was ~ 50-100 nm. These discrepancies are explained by the presence of microstrains in the atomic matrix of the sample, as well as instrumental factors. The microelemental analysis revealed practically perfect stoichiometry of ZnO grown on porous-Si/Si.

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Вирощування ZnO на підкладках макропоруватого Si методом ВЧ магнетронного розпилення

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Мета роботи полягала у дослідженні процесу утворення оксиду цинку методом ВЧ магнетронного розпилення на кремнієвих підкладках орієнтації (100) з попередньо нанесеною системою макропор. Зразки поруватого кремнію були отримані методом електрохімічного травлення. Було використано пластини Si (100) *n*-типу провідності. Осадження тонких плівок ZnO проводилося в ВЧ-розряді в середовищі аргону з киснем шляхом розпилення цинкової мішені. Мішень мала діаметр 80 мм і товщину 6 мм. Час осадження склав 1200 с. Тиск в камері вирощування підтримувався на рівні 10^{-3} Па. Температура підкладки була зафіксована на рівні 300 °C. Рентгенографічні дослідження ZnO показали, що плівки мають полікристалічну природу зі структурою типу вюрцит і гексагональною фазою. Кристаліти в покриттях ZnO були високо орієнтовані по осі *c* перпендикулярно до поверхні підкладки. Постійна решітки вздовж кристалографічної осі *c* плівки ZnO склала 5,2260 Å. Середній розмір кристалітів, розрахований за формулою Селякова-Шерера, становив 12 нм. Згідно СЕМ розмір зерен склав приблизно 50-100 нм. Дані розбіжності пояснені наявністю мікродеформацій в атомній матриці зразка, а також апаратурних факторів. Мікроелементний аналіз виявив практично ідеальну стехіометрію ZnO, вирощеного на поруватому Si/Si.

Ключові слова: Поруватий Si, Плівки ZnO, Метод ВЧ магнетронного розпилення.