Proc. Estonian Acad. Sci. Phys. Math., 2003, **52**, 3, 277–288

Atomic layer deposition of ZnO thin films and dot structures

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Received 20 January 2003, in revised form 31 March 2003

Abstract. Successful growth of thin films and quantum dots of ZnO by atomic layer deposition (ALD) is reported. Properties of ZnO films produced by four different ALD-procedures and by oxidation of ALD-grown ZnS films are discussed. We also shortly describe the use of thin ZnO films as buffer layers for GaN deposition.

Key words: atomic layer deposition, ZnO, GaN, thin films, quantum dots.

1. INTRODUCTION

We report a successful growth of ZnO films by atomic layer deposition (ALD) using simple, inorganic reaction precursors. ZnO films were obtained using double or single exchange chemical reactions, or by a synthesis reaction, i.e., from elemental components zinc and oxygen. We briefly describe properties of these ZnO films. We also obtained thin and amorphous ZnO layers by post-growth oxidation of ALD-grown ZnS films at temperatures higher than 500 °C. The crystalline ZnS films were grown by ALD by a double exchange chemical reaction ($ZnCl_2 + H_2S$) on either silicon or GaAs substrates. Their growth conditions and the resulting film quality are described elsewhere [1].

We also claim that the ALD-grown ZnO films grown on glass are suitable as nucleation layers (so-called buffer layers) for GaN epitaxy. We used low-temperature laser assisted chemical vapour deposition (LCVD) to deposit GaN layers on ZnO coated glass [2]. Subsequently a new method of obtaining of free-standing and crystalline GaN wafers was established. These wafers are suitable for homoepitaxial growth of GaN structures.

2. EXPERIMENTAL METHODS

Characterization techniques included cathodoluminescence (CL) and scanning electron microscopy (SEM). The CL spectra images were taken in a JEOL 35C scanning electron microscope equipped with a MonoCL2 CL system by Oxford Instruments. Cathodoluminescence emission was detected using Hamamatsu R943-02 Peltier cooled photomultiplier. The spectra were not corrected for the system's response, which may result in a small error in peak energies. All spectra discussed here were taken at room temperature. Charging effects were carefully minimized.

Quantitative information on the microstructure of surfaces of the samples was drawn from the atomic force microscopy (AFM) and high-resolution SEM images. The images were taken in a JEOL JSM-6300F scanning microscope with a field emission gun.

The micro-photoluminescence (micro-PL) spectra were measured with either a Renishaw micro-Raman system, with a resolution of 1.6 meV using a polarized 325 nm excitation at an excitation power density of 120 kW/cm^2, or UV micro-image system of Olympus Optical Co., equipped with a high-resolution (5.6 mln pixels) DP50 CCD camera. The PL emission spectra at single locations and emission maps, that is spatial distributions of emission from the sample, were taken at a spatial resolution down to 2×2 μm and were measured at room temperature. Photoluminescence experiments were performed at liquid helium temperature in a conventional PL set-up, using UV line of Coherent argon laser for a photo-excitation.

3. GROWTH METHODS AND PROPERTIES OF ZnO FILMS

A comprehensive review of ALD, often referred to as atomic layer epitaxy (ALE), is contained in [3,4]. We have recently employed this technique to obtain thin films of sphalerite-type ZnS [1,5], (Cd,Zn)S [6], and ZnSe [7], proving that the method is also suitable for growth of monocrystalline thin films. In particular, ALD-grown monocrystalline ZnSe films show very promising properties for possible opto-electronic applications [8].

Atomic layer deposition offers exceptional flexibility in the use of various precursor systems and reaction procedures. This was utilized in the present study employing four different procedures based on ALD reactions in the preparation

of thin ZnO films using an F-120 ALE reactor (Microchemistry). Glass, quartz, silicon ((0 0 1) and (1 1 1)), and GaAs (0 0 1) were used as substrates. We also used sapphire plates covered with epitaxial films of GaN by conventional metalorganic vapour phase epitaxy (MOVPE) as substrates. The growth rate was controlled by measuring interference patterns in optical absorption/transmission data for films grown on glass or quartz.

Initially, a reaction of zinc acetate with water vapour has been used to grow polycrystalline films of ZnO by ALD [9]. Later attempts involved hydrolysis of metalorganic precursors of zinc [10]. Oxidation of zinc with NO_2 has been also tested to obtain ZnO films on the GaN substrates [11]. In our approach we used very simple, low costs and easy in use inorganic precursors and grew ZnO by four different methods, with nitrogen as transport gas at 5 mbar, with 4000 sequential ALD cycles of about a second each. Conditions for each of the methods listed below were slightly modified.

In the first attempt, we applied a double exchange reaction $ZnCl_2 + H_2O \rightarrow ZnO + 2HCl$, with $ZnCl_2$ at a temperature of 390 °C and the substrate temperature of about 500 °C. The method produced ZnO films of moderate quality as observed in SEM and AFM studies. In the second approach we used two versions of a single exchange chemical reaction. We either used metallic Zn source and water vapour (from liquid source) $Zn + H_2O \rightarrow ZnO + H_2$, at a slightly reduced substrate temperature to about 430 °C, or $ZnCl_2$ and oxygen, with $ZnCl_2$ at a temperature of 390 °C and the substrate temperature of 480 °C. In the fourth process we used a synthesis reaction, i.e., we used metallic Zn and oxygen gas ($2Zn + O_2 \rightarrow 2ZnO$), at a substrate temperature of about 430 °C. A relatively good morphology of the films was obtained for each method, but with low growth rates of about 50–200 nm in 4000 cycles, depending on the procedure used.

We also obtained ZnO films by oxidation of ZnS. We first grew mono-crystalline ZnS films, by the method described in [1,5]. Then we applied post-growth annealing in oxygen flow at a temperature of about 550 °C, producing thin films of ZnO on top of ZnS. For films grown on quartz, we could observe a shift of the fundamental absorption band and the additional interference patterns, confirming the oxidation of the ZnS film. In addition, "edge" ZnO PL of an excitonic origin appeared after film annealing, as shown in Fig. 1. The ZnO films thus obtained were, however, fully amorphous, which is probably due to a complicated oxidation mechanism. Very rough surfaces were observed in SEM, AFM, and micro-PL, as shown in Fig. 2.

Structural and spectral properties of ZnO films were studied with X-ray diffraction, SEM, AFM, and optical methods (CL and PL). X-ray data will be published separately [12]. Here we shortly describe SEM, AFM, and optical investigations. The best-quality films were obtained for sapphire substrates covered with MOVPE-grown GaN films. The obtained ZnO layers were crystalline and showed very smooth surfaces, with the average roughness of 0.45 nm [12]. The properties of these films will be described in a forthcoming publication [12] and are

not discussed here. ZnO films of a relatively good quality were also obtained using GaAs or ZnS/Si as substrate materials. Film deposition on silicon covered with a thin layer of SiO_2 resulted in rough surfaces and three-dimensional growth.

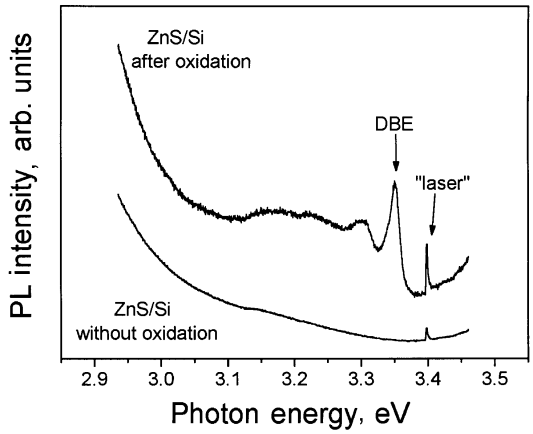


Fig. 1. Low-temperature photoluminescence (PL) spectra of the ZnS film grown by atomic layer deposition on silicon, taken before and after oxidation. The upper curve, taken after annealing the sample at a temperature of 550 °C, shows the appearance of ZnO "edge" emission of excitonic origin, attributed by us to radiative recombination of donor bound excitons (DBE).

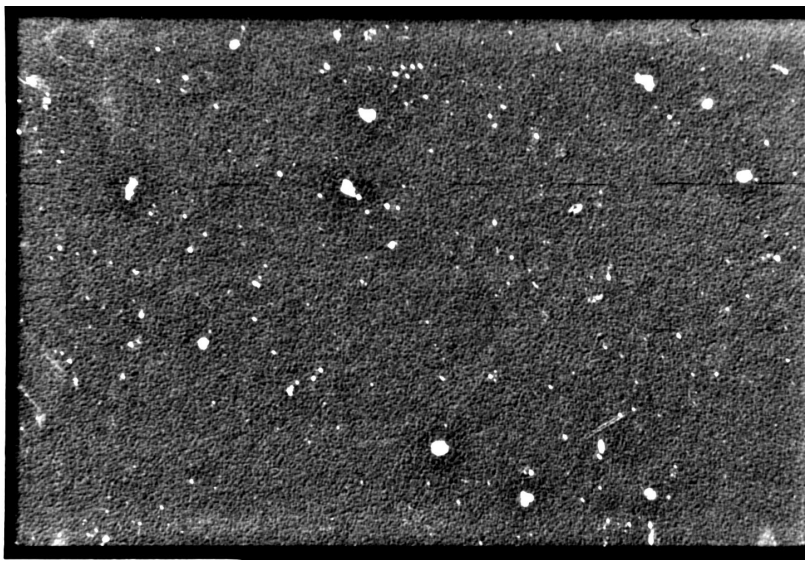


Fig. 2. Micro-photoluminescence image taken with Nomarski microscope showing surface morphology of an oxidized ZnS film. The ZnS film was grown by atomic layer deposition on (1 1 1) silicon substrate using a double exchange chemical reaction and was post-growth annealed in oxygen flux.

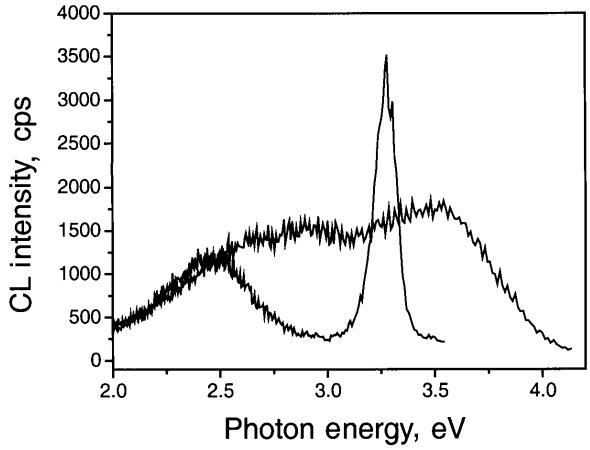


Fig. 3. Room temperature cathodoluminescence (CL) of two ZnO films grown by atomic layer deposition using single exchange chemical reaction. Sharp excitonic "edge" CL is observed for the film grown on ZnS/(1 1 1) Si. We also show broad and weak CL of the ZnO/GaAs film showing a rough surface and three-dimensional growth mode.

As an indication of good spectral quality of our films is the observation of relatively sharp room temperature "edge" emission of an excitonic origin, as shown in Fig. 3 from the CL studies. On the basis of a separate study of bulk ZnO samples we attribute the observed "edge" emission to a radiative recombination of excitons bound at neutral donor centres. This observation agrees with n-type conductivity of our ALD films. The origin of an abundant donor impurity remains unknown. Sharp excitonic emission was only observed for films grown by the two single exchange chemical reactions and for ZnO films grown on either GaAs or ZnS/Si substrates. In samples with rough surfaces the excitonic emission was very broad and weak (see Fig. 3) or not observed, and the PL and CL spectra were dominated by a very strong red emission band, not shown in Fig. 3.

4. GOLD AND SILVER AS SURFACTANTS FOR THE GROWTH OF ZnO QUANTUM-DOT-LIKE OBJECTS

In the case of single exchange chemical reactions and in the synthesis reaction a three-dimensional growth mode was often observed, especially if we used uncoated silicon as a substrate. In general, the growth mode and growth rate depended on the choice of the substrate. Only for sapphire/GaN substrate the ZnO films were flat and the two-dimensional growth mode dominated [12]. For (1 1 1) silicon as a substrate a thin layer of ZnO was first grown, with a microgranular microstructure, as observed in AFM (Fig. 4). This was followed by a growth of three-dimensional irregular islands, reaching a few hundreds of

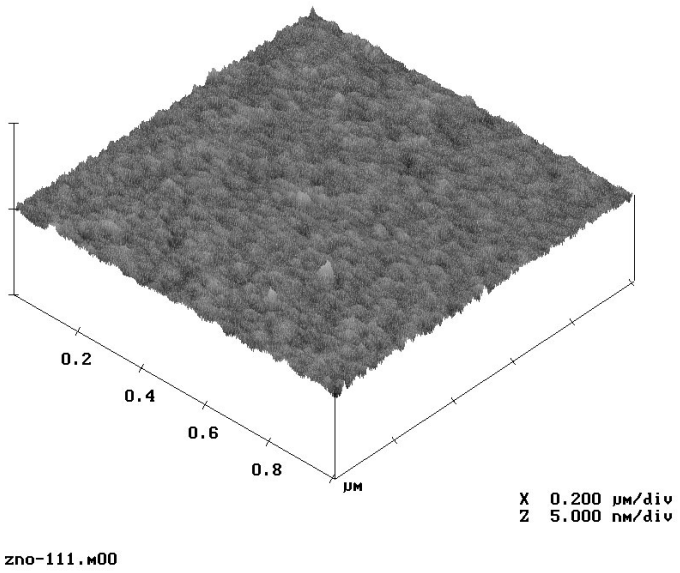


Fig. 4. Atomic force microscopy image of ZnO film obtained by atomic layer deposition using a single exchange chemical reaction on (1 1 1) silicon substrate.

micrometres in size. These islands show a relatively bright edge emission even at room temperature, which is not observed from a coating film and smaller islands (Figs. 5 and 6). Figure 5a, b show micro-PL images taken at the same region of the ZnO layer with two low pass filters, blue (a) and UV (b). The "edge" PL is observed only from larger islands (see Fig. 5b), the smaller ones show "deep" red-green PL emissions. No PL was observed from thin ZnO regions with a microgranular structure. We used CL to detect the emission spectra from these islands. First we found islands in the SEM images and then, using the so-called spot-mode CL, we excited the CL emission of these islands with electron beam. A sharp "edge" excitonic emission was observed, as shown in Fig. 6 for the Si/Ag/ZnO system. Similar CL spectra were observed for other samples showing islands.

A very different film morphology was observed for silicon substrates covered with a thin layer of either gold (3 nm) or silver (5 nm) prior to the ALD process. Thin films of Au or Ag act as surfactants. Dot-like objects were formed when the surface of the films was covered fairly uniformly (Figs. 7 and 8a, b). The density and average size of these objects depended on the metal used. Larger dots (up to 200 nm, Fig. 8b) were observed for the Ag coating of (1 1 1) silicon, smaller dots (about 50 nm) for the Au coating. The latter system showed evidence for a quantum confinement of carriers and excitons. The above band gap emission of ZnO was recorded in the spot-mode CL study, using low acceleration voltage and setting the excitation beam on dot-like objects. The emission observed is shown in Fig. 6, together with excitonic "edge" CL of larger islands. These dots were

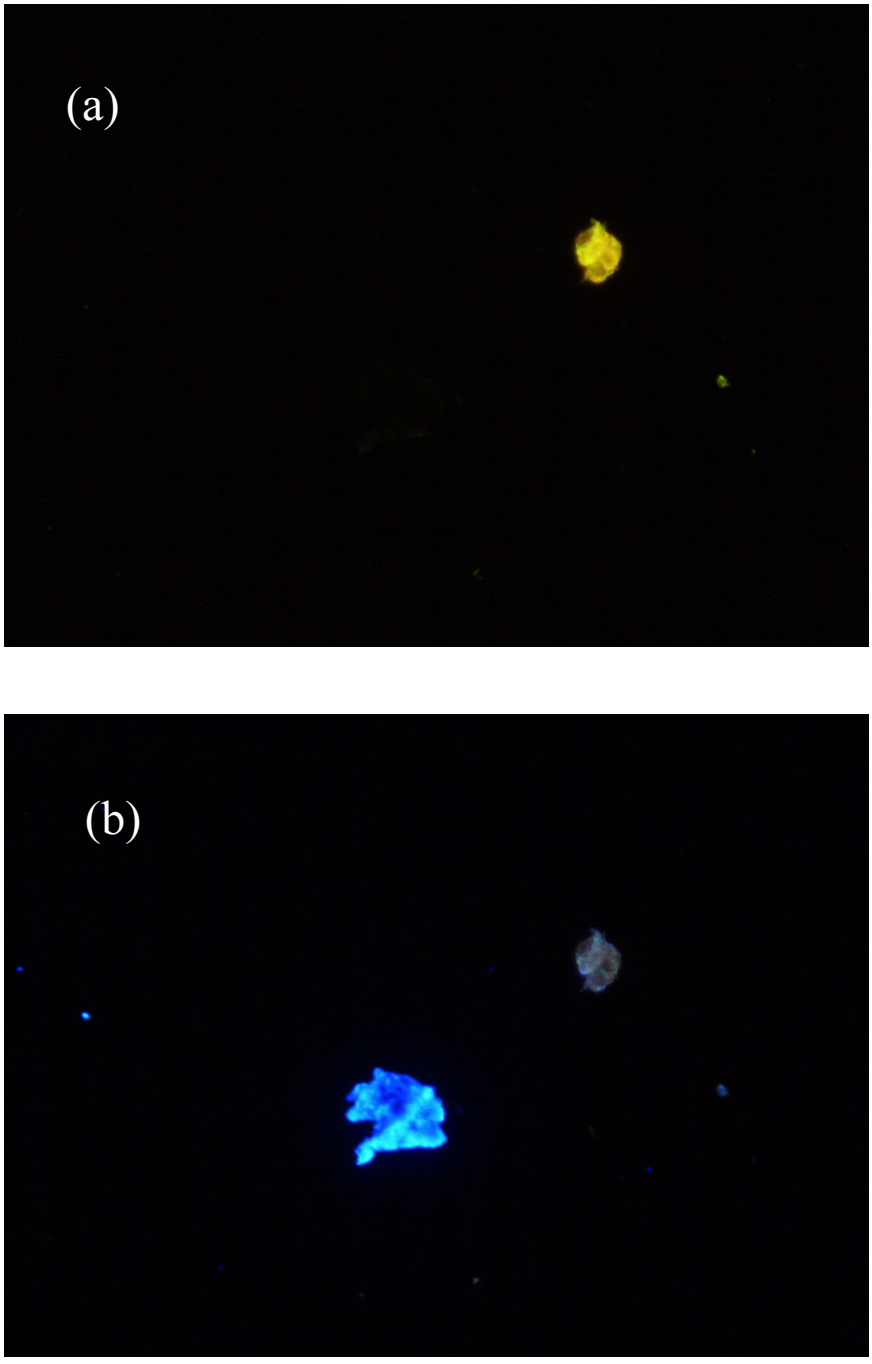


Fig. 5. Micro-photoluminescence (PL) images of the thin ZnO layer grown by atomic layer deposition using a single exchange chemical reaction. Image (a) was taken with a blue low pass filter, (b) with a UV low pass filter. The "edge" PL of ZnO is observed only from larger islands.

stable, no maturing occurred even after relatively long time, also in the case when dots were not covered with a cap layer.

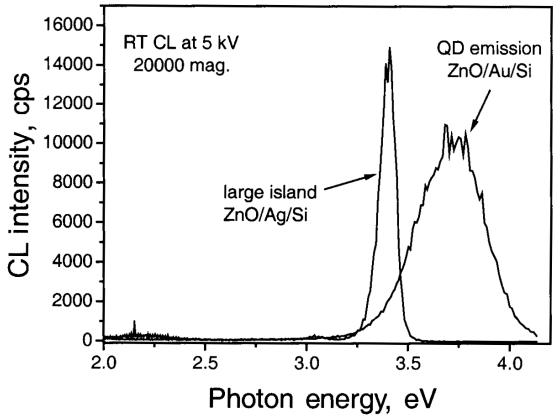


Fig. 6. Spot-mode cathodoluminescence (CL) spectra of two ZnO samples grown on (1 1 1) silicon covered with Ag or Au thin layers. Emission of CL from a large island, observed in the ZnO/Ag/Si sample, and from quantum dot (QD) objects in ZnO/Au/Si is shown.

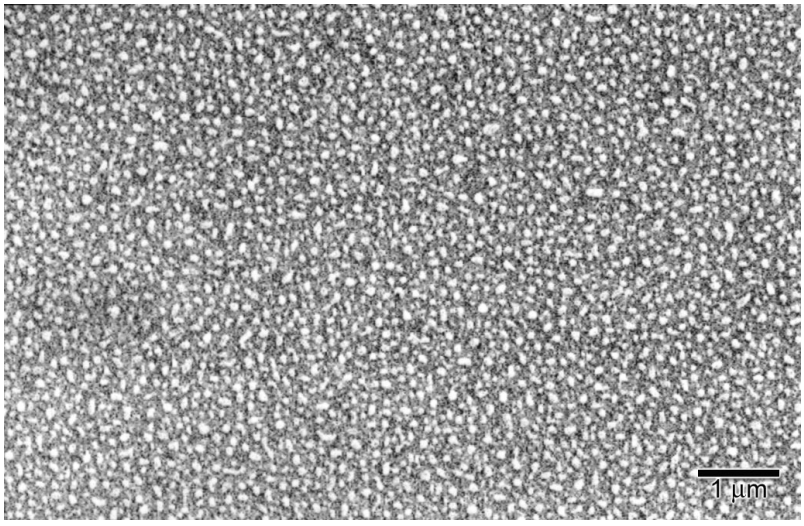
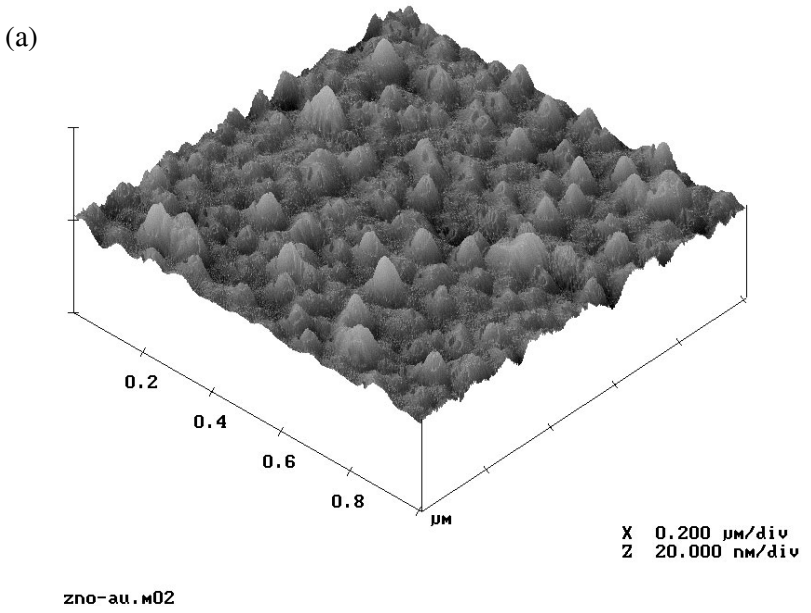


Fig. 7. Scanning electron microscopy image of a relatively large area of the ZnO/Ag/Si (1 1 1) film taken at room temperature.



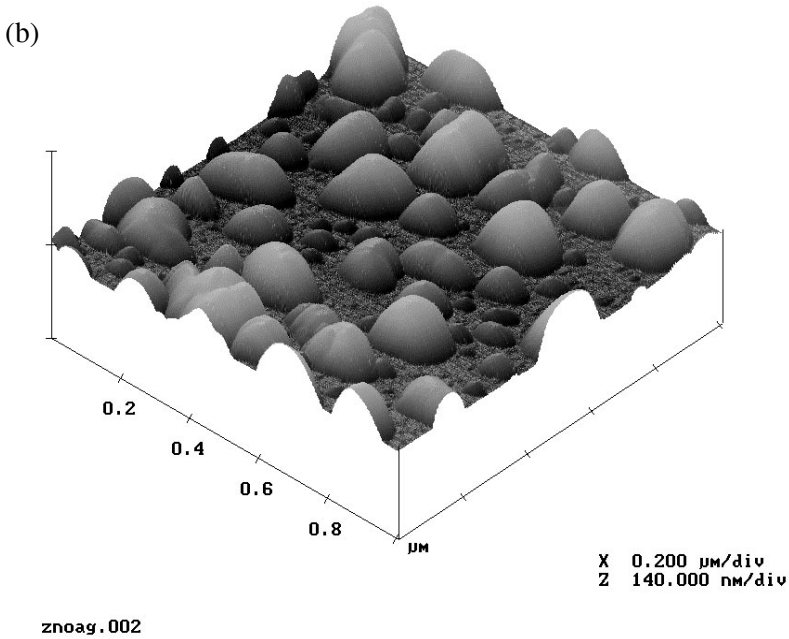


Fig. 8. Atomic force microscopy images of ZnO dot-like structures grown by atomic layer deposition using a single exchange chemical reaction on (1 1 1) silicon substrate covered with a thin layer of Au (a) and Ag (b).

5. GaN DEPOSITION ON ZnO/GLASS SUBSTRATE OBTAINED BY ATOMIC LAYER DEPOSITION

We have recently employed a low-temperature LCVD technique using remote plasma enhanced laser induced chemical vapour reaction to grow thick GaN films on soda lime glass covered with a buffer ZnO film deposited with ALD [2]. The use of a low-temperature version of MOVPE was crucial, since ZnO is not resistant to ammonia treatment for temperatures higher than 650°C. In turn, the use of ZnO buffer initialized correct nucleation of the GaN layer. Even though the GaN films obtained this way were polycrystalline, they have shown relatively good structural and electrical properties, as described in [2]. Freestanding layers of GaN were obtained by etching away the glass substrate and ZnO buffer layer. The freestanding GaN layers were polycrystalline, but could be recrystallized by low-temperature (below 570°C) annealing. A crystalline structure of these films was verified with the X-ray diffraction technique [2]. We also used silicon and GaAs substrates covered with thin ZnO films as substrates in molecular beam epitaxy (MBE) of GaN. The properties of these films are discussed separately [13].

6. CONCLUSIONS

Thin films of ZnO were grown by ALD using several variants of the method and simple, inorganic precursors. ZnO films grown on sapphire covered with GaN are crystalline. In the case of ZnO deposition on silicon substrate island-like growth is often observed. The use of gold or silver as coating of silicon resulted in the formation of dot-like objects, showing (in the case of ZnO/Au/Si) quantum confinement effects. The ZnO films grown by us were used as buffer layers in MBE and LCVD growth of GaN epilayers. In particular, freestanding and crystalline GaN substrates were obtained, which can be used in homoepitaxial growth of GaN-based structures.

ACKNOWLEDGEMENTS

This work was partly supported by grant No. PBZ-KBN-044/P03/2001 of Polish State Committee for Scientific Research (KBN). F-120 ALE reactor of Microchemistry was bought using SEZAM grant of the Foundation for Polish Science.

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ZnO õhukeste kilede ja punktstruktuuride aatomkihtsadestamine

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On kirjeldatud ZnO kilede ja kvantpunktide kasvatamist aatomkihtsadestamise meetodil ning iseloomustatud neljas aatomkihtsadestamise protsessis sünteesitud ja aatomkihtsadestatud ZnS kilede oksüdeerimisel saadud ZnO kilesid. ZnO kilesid saab kasutada ka puhverkihtidena GaN kasvatamisel.