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Selective homoepitaxial growth and luminescent properties of ZnO nanopillars

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Abstract

High-spatial density ZnO nanopillars (NPs) have been fabricated on catalyst- and pattern- free Si wafers using atmospheric pressure metal organic chemical vapor deposition (APMOCVD) at a moderate temperature (500 °C). The nanopillar diameter is ~ 35 nm and length is ~ 150 nm with a density of $\sim 2 \cdot 10^9$ cm⁻². The growth evolution of the nanopillars, providing the $(0001)_{\text{NP}} \parallel (0001)_{\text{ZnO grain}} \parallel (100)_{\text{Si surface}}$ epitaxial relationship is extensively studied by scanning and high resolution transmission microscopy. The approach of obtaining the ZnO 1D structures is explained in terms of selective homoepitaxial growth via the crystallographic anisotropy of the seeding layer. The advanced PL properties of ZnO NP's, e.g indications of free excitonic and absence of defect emission, are related to their single crystalline nature within one pillar and most probably better stoichiometry and less contamination. The observed efficient monochromatic UV emission from the ZnO NP's at room temperature points toward their potential application as building blocks for nanoscale optoelectronic devices.

PACs: 61.46.Hk, 68.37.Lp, 61.46.Km, 61.72.Ff, 78.67.Qa

1. Introduction

ZnO has one of the largest families of nanostructures; low-sized objects of various shape, size, and arrangement have been reported for the last decade [1-3]. Particularly, elongated ZnO nanostructures (nanorods, nanopillars, nanoneedles, etc) are of extreme attention due to their high crystallinity and hence high charge carriers mobility, low concentration of non-radiative defects and technological compatibility. The realization of vertically well-aligned 1D ZnO nanorods is very important for application in nanoscale light-emitting diodes (LEDs) [4, 5], sensors [6], piezogenerators [7] and field emitters [8-10]. However, an additional important issue has to be solved. Due to the key role of Si in the semiconductor industry, it is prospective to integrate devices based on ZnO with Si for an enhanced functionality. The well ordered growth of ZnO 1D structures of controlled structural, optical and electrical properties is a key issue in terms of novel 3D nanoarchitecture. At present it is still challenging to grow well-ordered highly oriented low-dimensional ZnO nanostructures on commercially available low-cost Si substrates. Moreover, such structures need to possess size and spatial uniformity with well controlled in-between distance, and have to be of high structural and optical quality. Therefore, in the new-coming bottom-up technology the selective growth which permits the position, size, and morphology of semiconductor nanostructures to be controlled is a prerequisite for the integration of nanodevices [1, 11].

Until now, a number of reports has been published concerning successful growth of ZnO nanopillars on various substrates [12-15], including Si [16-19] by different techniques [17, 18, 20, 21], via catalyst assisted or catalyst free approaches [12, 16, 20, 22-24]. However, the use of catalyst can be detrimental for the subsequent device fabrication [25]; equally a sophisticated pattern preparation makes the approach non-prospective for the industry. The idea of selective growth by using the buffer layer anisotropy was partially expressed earlier [14, 16-18, 21], but the size of the structures still has to be further decreased. Additionally, there is a lack of information about the growth mechanism. Therefore, the detailed understanding of the growth process of ZnO nanopillars on a Si substrate is an open issue.

In this paper we report catalyst- and patterned-free growth of ZnO nanopillars (ZnO NP's) by metal organic chemical vapor deposition at atmospheric pressure on Si substrates at moderate temperatures. We have investigated the nucleation of the ZnO NP's on selected *c*-axis oriented crystallites of a seeding layer. By utilizing the ZnO seeding layer crystallographic anisotropy a selective homoepitaxial growth of ZnO NP's is taking place. It is shown that at the appropriate layer thickness and optimal growth rate NP's of low size (diameter ≈ 35 nm and length ≈ 150 nm) are obtained, being of high density ($\sim 2 \cdot 10^9$ cm⁻²), ordered and oriented with their *c*-axis perpendicular to the Si substrate. Via comparison to a bulk ZnO crystal, the advanced luminescent properties of the as-grown ZnO NP's are confirmed: the intense free-excitonic emission in the UV range of spectra was observed at the absence of visible luminescence from defect levels.

2. Experimental details

The ZnO growth was performed by simplified version of metal organic chemical vapor deposition at atmospheric pressure (APMOCVD) using Zn β -diketonate (acetylacetonate $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, Sigma Aldrich) as a single source ZnO precursor and Ar as a buffer gas. Details of the APMOCVD growth can be found elsewhere [11, 15]. The ratio between the Zn and O was maintaining constant due to the single source nature of the precursor used. The Zn and O partial pressures were controlled by the precursor evaporation temperature, ranged between 120 and 160 °C. Si (100) wafers were used as substrates without employing a metal catalyst or any surface patterning. The substrates were pre-cleaned by washing in acetone and ethanol for 5 min at 80 °C, followed by nitrogen flow drying. A seeding layer was grown at an optimized temperature and time to form c-oriented grains with a growth rate of about 3 Å/s. The optimized thickness of the seeding layer was found to be 200 nm. At a second stage nanopillars were grown at 500 °C while the Zn and oxygen partial pressures were decreased twice from the initial values yielding a growth rate of ~ 1.5 Å/s. This we refer to in the following as a low growth rate.

Scanning electron microscopy (SEM) was used to image the grown 1D ZnO. The Leo 1550 Gemini SEM was operated at voltage ranging from 10 to 20 kV and standard aperture value 30 μm . Microstructure study was carried out using conventional and high-resolution transmission electron microscopy (HRTEM). For cross-section transmission electron microscopy (XTEM) specimen preparation, two strips of the specimen were cut and glued face to face, and then were mechanically thinned down to 25 μm . Subsequently the specimens were thinned to electron transparency by Ar ion milling with energy of 4 kV, at a low incident angle of 4° in order to avoid amorphization artifacts from the argon ions. For the conventional characterization a TEM JEM 120 CX was used, while for the HRTEM investigation a JEM 2011 having 0.194 nm point-to-point resolution was utilized. The emissive properties of the ZnO nanostructures were investigated by micro-photoluminescence, carried out at a low (10 K) and room temperatures with the frequency doubled Nd:YVO 4 laser as continuous wave excitation source, giving the wavelength $\lambda=266$ nm. The emitted luminescence was collected and mirrored into a single grating 0.45 m monochromator equipped with a liquid nitrogen cooled Si-CCD camera with a spectral resolution of about 0.1 meV. The excited area was around 10 μm in diameter providing an excitation density of $2 \div 400$ W/cm². A bulk ZnO crystal from ZnOrdic [26] was used as a reference for the comparison of the optical properties. Cathodoluminescence (CL) spectra were measured at room temperature in the Leo 1550 Gemini SEM using a 10 keV electron beam and 30 μm of aperture with 1800 lines mm⁻¹ grating. Panchromatic images of the samples were taken to reveal local features of the emission intensity.

3. Results and discussion

3.1. Effect of the anisotropy of the seeding layer on the ZnO nanopillars growth

Since the aim of this study was to grow low size ZnO nanostructures, the seed layer characteristics, as the most essential factor, were investigated in details. As observed earlier, the ZnO growth on lattice mismatched substrates (e.g. Si) resulted in a polycrystalline layer deposition. The polycrystalline layer consists of grains of certain size, which are specifically oriented toward the substrate plane [27]. The layer morphology is determined by the grain size and texture. The grain size is dependent on the growth temperature (T_g); while the texture depends on both the temperature and time of growth. We have investigated thin seeding layers of ZnO, deposited at temperatures ranging 300 – 500 °C. The results showed that as low is the temperature of deposition, as high is the nucleation density; however, decreasing of substrate temperature degrades the film c-texture. Both grain size and c-texture of the ZnO film increase with the substrate temperature and films thickness. Thus, one can use the growth temperature and layer thickness to control the density of the overgrown nanopillars. The most optimal seeding layer was found to be grown at 500 °C as a polycrystalline layer, of mosaic structure, with a crystallite size of ~ 150 nm (for layer thickness up to 200 nm) and a developed texture along the c-axis (figure 1(a)).

In order to achieve an ordered growth of ZnO nanopillars of low size, the following growth strategy was applied. The growth procedure comprises two-steps: i) heteroepitaxial deposition of a thin polycrystalline seeding layer (~ 200 nm) at moderate Zn and O partial pressures and growth temperature $T_g = 500$ °C and ii) *homoepitaxial* growth of ZnO NP's at the same temperature, but lower Zn and O partial pressures. At this stage the value of the precursor pressure was optimized for the growth of ZnO NP's of the lowest possible diameter. Figure 1(b) shows an overview of the low sized ZnO NP's at the initial stage of their growth. The individual NPs are of a uniform shape and size over the whole surface with an average diameter and height of about ~ 35 nm and ~ 150 nm, respectively. They are densely located over the surface (~ $2 \cdot 10^9$ cm⁻²) and are elongated along their c-axis perpendicularly to the substrate plane. Continuation of the growth resulted in an array of ZnO NP's (Figure 1(c)).

Assuming that the characteristics of the seeding layer are decisive for the ZnO NP formation, we have investigated the microstructure of the seeding layer (grown at 500 °C) by taking plan-view TEM images from the substrate side. For this purpose, the Si substrate was partially removed by thinning the specimen from the backside (figure 2(a)). The seeding layer consists of polycrystalline grains, which exhibits well developed hexagonal facets, according to the corresponding diffraction pattern in figure 2(b). The strong preferred orientation is evident by indexing the diffraction rings in the figure. The rings ($1\bar{1}00$), ($1\bar{1}01$), ($11\bar{2}0$) and ($1\bar{1}02$) were identified, figure 2(c). However the (0002) ring, which should be located between ($1\bar{1}00$) and ($1\bar{1}01$) rings was missing because the (0002) lattice planes are almost perpendicular to the electron beam and consequently they cannot satisfy the Bragg condition. Thus, the SAED (selective area electron diffraction) pattern taken from the substrate proves that the seeding layer is of a

polycrystalline nature. We have also studied individual grains from the seeding layer (figure 3); some of the crystallites are well faceted and are oriented with their $(11\bar{2}0)$ crystallographic plane corresponding to the (110) plane of the Si substrate. The SAED image taken from the individual grain proves that the c-axis of the crystallite is perpendicular to the substrate plane (shown as the inset in figure 3). The evolution of the seeding layer and the separate grain into nanopillars was also studied by TEM and is depicted in figure 4. The results reveal that the seeding layer consists of different types of crystallites with a mean height from the top to the interface ~ 115 nm and a mean width ~ 160 nm, (figure 4(a)). The conical crystallites exhibit strong preferred orientation having the c-axis almost perpendicular to the Si-substrate. The crystallites have the conical shape, further labeled as type A-crystallites. As it will be further demonstrated, the only A-type crystallites promote further growth of ZnO NPs. Worth noting is that growth of the grains, oriented with their c-axis *not* perpendicular to the substrate is depressed, and they did not result in further growth. The corresponding selected area diffraction (SAED) pattern taken from this grain including also the Si substrate, reveals that the $(11\bar{2}0)$ crystallographic plane of the ZnO corresponds to the (110) plane of the Si substrate, inset of the figure 4(a). The preferred orientation of the conical grains was also confirmed by high resolution cross sectional TEM (XTEM) micrographs, where the (0001) ZnO lattice planes from a conical crystallite are evident (figure 4(b)). Lattice planes of $(0001)^*$ type with periodicity 0.52 nm which are parallel to the substrate are shown in the inset of the figure. The forbidden $(0001)^*$ ZnO lattice planes that have double periodicity of the (0002) ones are observed due to double diffraction. The top part of the nanopillars was not observed by XTEM for two reasons. The very thin top part of the ZnO NPs was broken during the XTEM specimen preparation, which involves pressing the two parts of the sample face-to-face. Also, during the Ar ion milling the very thin tips of the NPs are worn down first. Nevertheless, by analyzing the available TEM and SEM images, it is possible to conclude that the nanopillars are extensions of the conical crystallites and exhibit a strong $[0001]$ preferred orientation almost perpendicular to the substrate. We assumed that the nanopillar growth is promoted on energetically selected crystallites and the lowest energy plane will be favored. Each pillar is positioned on the apex of the conical part of the grains labeled A. Thus, namely this type of crystallites origins the ZnO nanopillars during further growth. An intermediate amorphous zone between the Si and the ZnO seed layer, about 4 – 6 nm thick, was observed. Since the thickness of this layer is too large to consider it as a native oxide (normally of 1 – 2 nm), we suggest that the native oxide was further extended by SiO_x growth during the ZnO deposition. This layer can have a detrimental influence on the luminescence properties of ZnO, causing the so called “green-yellow” luminescence due to oxygen vacancies [26, 27].

Focusing on the NP formation mechanism the following explanation can be proposed. The growth process of ZnO NPs consists of two stages. The 1st stage is a material deposition on highly mismatched substrates (in-plane lattice mismatch between the ZnO and Si is $\approx 40\%$ [28]). At the moderate Zn and O pressures in our experiments, a high nucleation density takes place and a polycrystalline film is formed. According to the nucleation theory, the density of nucleation is determined by the growth temperature and the activation energy of nucleation ΔG^* , which is

composed of volume free energy ΔG_v and surface free energy ΔG_s [29, 30]. The layer is *polycrystalline* and consists of single-crystal grains, randomly in- and out-of-plane oriented with respect to the substrate plane (see figure 5(a)). Such a crystallographic anisotropy of the layer is *reflected* by a different surface free energy values for the main crystallographic planes of hexagonal ZnO: $G_{001}=-2.8102$ kJ/mol, $G_{101}=-2.1067$ kJ/mol and $G_{100}=-2.0013$ kJ/mol, respectively [31]. At this stage the specific number of the grains with their c-axis oriented perpendicularly to the substrate (c-texture degree) is mainly determined by the growth temperature. However, because of the lowest surface free energy of (001) crystallographic plane, the increase of the layer thickness improves its c-axis texture. At the same growth conditions, a further increase of the layer thickness results in a conventional polycrystalline film. That is a common mechanism of competitive growth of polycrystalline films [32].

In our case, the 2nd step is *homoepitaxial* growth of ZnO following the crystallographic anisotropy of the seeding layer. By decreasing the Zn and O pressures, the growth mode is switched into *selective* 1D growth. Due to sufficient temperature and lower species density the surface diffusion of the atoms is high, which enables them to occupy the most energy favorable sites. Since the (0001) crystal plane has the lowest surface energy and therefore the smallest attachment energy [33 - 35], it is energetically most favorable for atoms to build up only grains of a certain orientation, with the (0001) plane parallel to the substrate surface (figure 5(b)). At low Zn and O partial pressures and due to the fastest growth rate along the c-axis, elongated ZnO nanocrystals are formed – ZnO nanopillars. Inheriting the “mother grain” crystal orientation the ZnO NPs grow with their c-axis perpendicular to the substrate plane, providing the $(0001)_{NP} // (0001)_{ZnO \text{ grain}} // (100)_{Si \text{ surface}}$ relationship. Such a *selective* homoepitaxial growth results in an array of densely located low-size ZnO NP's (figure 5(c)).

3.2. Optical properties of the ZnO nanopillars vs bulk ZnO

Cathodoluminescence (CL) is used as an informative tool for characterization of the light emitting ability of semiconductors. The room temperature CL spectra of ZnO NPs possess only one intense narrow peak at $E \approx 3.3$ eV (figure 6). In order to clarify that the observed luminescence signal comes mainly from the ZnO nanopillars, not the seeding layer, we acquired a top-view panchromatic CL image. As it can be seen (the inset in figure 6), the light emitting spot size corresponds to the NP's diameter, earlier observed by SEM. Hence, we can conclude that the ZnO NPs mainly contribute to the light emission. Moreover, the room temperature luminescence spectra of ZnO NP's possess solely the emission peak in the UV range of spectra. Any additional peaks, for example from deep level defect emission in the visible region were not observed. The features of the luminescence of ZnO NPs in comparison to a bulk ZnO crystal were additionally studied by low temperature photoluminescence (LT PL) measurements (figure 7(a)). The optical properties of the ZnO bulk crystal as a reference were investigated by the same technique and instrument (figure 7(b)).

The 4K PL spectrum from ZnO NPs is shown in figure 7(a), the PL intensity is presented in logarithmic scale. According to earlier reports, the most prominent peak at 3.3643 eV is attributed to emission from a neutral-donor-

bound-exciton (D^0X) and the most probable reason for the peak can be H impurity [28]. The peaks at 3.3033 eV and 3.2242 eV are respectively the 1st and 2nd longitudinal optical (LO) phonon replicas of the neutral-donor-bound-exciton. Additionally from the high energy side the spectra possess two weak peaks, located at approximately 3.3732 and 3.3784 eV, which can be attributed to an ionized donor bound exciton and free-exciton emission (D^+X and FX_A respectively) [38, 39]. The signal of the free exciton is hardly distinguishable on the intense D^0X peaks shoulder at the low temperature. However, as we observed, with the increase of the temperature, the free excitonic peak became stronger and after the 160 K it totally dominates over the PL spectra, followed by its 1st and 2nd phonon replicas. The peaks at 3.314 eV and 3.2406 eV are respectively the 1st and 2nd longitudinal optical (LO) phonon replicas of free excitonic emission peak, separated from it and between each other with an energy ~ 70 meV [28]. At the lower energy side, a peak at 3.3268 eV is present, which, according to the literature data [3, 28, 39, 40], can be assigned to the two electron satellite (TES).

The high energy shoulder of the LT PL spectra of bulk ZnO, shown on figure 7(b), contains the peaks, which are assigned as FX_B and FX_A . They are assisted by two broader peaks from the low energy side, assigned respectively as first and second longitudinal replica of free exciton – $1LO_{FXb}$ and $2LO_{FXb}$. The energy difference between the original free exciton peak and the replicas is around 70 meV, what agrees well with the bound exciton energy value for ZnO [28]. The two peaks between the free neutral donor bound excitons (3.3693 and 3.3664 meV) are assigned to I_1 and I_3 [28] respectively. Their origin is not clear and can be explained by the presence of unidentified impurities during the growth process. The most intense peak is denoted as I_4 and can be assigned to a neutral donor bound exciton (D^0X) due to H presence in the ZnO [28]. The 1st and 2nd LO replicas are presented and their intensity decrease replicating the D^0X behavior. Moreover, the two electron satellite peak (TES) is located next at 3.328 eV. The energy difference between D^0X and TES is around 34 meV, what is close to two electron satellite separation energy reported for ZnO earlier [28, 40].

Thus, we would like to conclude that the ZnO NPs, being prepared on the foreign substrate and at rather low growth temperature, possess optical properties comparable to that of bulk ZnO crystals. Both spectra exhibit peaks, peculiar for ZnO: specifically, availability of free exciton emission at low temperature proves the high optical quality of the material. While observation of the phonon replicas, especially at elevated temperatures, confirms the high structural quality. The absence of the deep level defect emission from the ZnO NPs is an additional advantage over the number of earlier reported zinc oxide nanostructures, films or bulk crystals [41]. We believe, that such an advanced PL properties of ZnO NPs – indications of free excitonic and absence of deep level defect emission - are related to their single crystalline nature within one pillar and most probably better stoichiometry and less contamination due to the lower growth temperature. Earlier it was shown that nanostructures with a developed surface possess poor emission properties, explained in terms of increased surface recombination rate and believed to detriment the LED efficiency [42]. Despite the high surface-to-volume ratio of ZnO NPs it was confirmed that the light emission occurs mainly due to excitonic emission. Since excitons are a sensitive indicator of the material quality, it

additionally confirms the possibility to grow low size well ordered ZnO structures with improved optical properties. Furthermore, the exciton-related recombination process can be utilized for optoelectronic devices fabrication, operating at RT.

The practical importance of this work is the demonstrated growth approach leading to fabrication of ordered low sized ZnO nano-objects, densely arranged on plane of a silicon substrate. The key novelty of the applied growth approach is utilization of the intrinsic material properties at certain conditions, enabling the surface engineering on nanoscale. Despite the size of the ZnO NPs is still far from the scale where quantum phenomena can be expected (for example, a Bohr radius of ~ 2 nm [2]) it fits well with the size mediated material properties (for ex. typical Debye length $\sim 50 - 100$ nm for ZnO [43]). Moreover, it coincides well with the size limits of the characteristic size and may fulfill the requirements of scalability of the 32 nm technology node [44]. The size uniformity is an essential accomplishment here. Along with the NP's length uniformity it creates valuable grounds for expanding the "bottom up" technology [40]. An additional proof for the viability of the reported technique and fabricated structures is the demonstration of their functionality. It has been shown that the field emission properties result from the size and arrangement of the NPs [45]. Advanced light emission from the NP's is due to their high crystalline quality, expected low strain and stress, inherited from the free-standing growth of the individual NP's. The importance of the growth approach lies in the possibility to grow low scale ordered ZnO NP's by conventional technology in one run on low cost lattice matched substrates. Control of the location of the low sized well ordered ZnO objects via the fundamental material properties is a key issue of this approach and can serve as a powerful mean for the hierarchical growth of novel semiconductor materials.

4. Conclusion

In conclusion, we have shown the possibility to fabricate arrays of densely located, ordered ZnO nanopillars on commercially available low cost Si substrates by APMOCVD via selective homoepitaxial growth. It is shown, that due to the crystallographic anisotropy of the polycrystalline seeding layer, the growth of 1D ZnO is promoted on c-axis oriented sharp tipped seeding layer grains, enabling spatially selective growth. At an appropriate layer thickness and optimal ratio low sized NPs (diameter ≈ 35 nm and length ≈ 150 nm) are obtained, being of high density ($\sim 2 \cdot 10^9$ cm $^{-2}$), well-ordered and oriented with their c-axis $\perp$ Si substrate. The grown ZnO NPs demonstrated a noticeable light emitting ability at RT, possessing an intense peak of UV emission and absence of defect luminescence in the visible range of spectra. At low temperature ZnO NPs demonstrated well-developed low photoluminescence spectra with characteristic features that have been observed for bulk material. Despite the developed surface and high surface to volume ratio, the nanostructures revealed an efficient excitonic emission, which makes them prospective for nanoscale LED design.

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- Figure 1.** SEM images, illustrating the morphology evolution from the seed layer, grown at 500 °C (a) (plane view) to the initial stage of the selective homoepitaxial growth of ZnO nanopillars (b) (45 ° tilted view) and final ZnO NP's structure (c), (plane view).
- Figure 2.** (a) Substrate side plan-view TEM image of the seeding ZnO layer on Si ($T_g = 500$ °C); (b) corresponding diffraction pattern, taken at large SAD aperture, including several crystallites; and (c) indexing of the diffraction rings in (b).
- Figure 3.** Higher-magnification TEM image of an individual ZnO crystallite consisting the seeding layer (type A) with the corresponding SAED pattern inset (the view is from the substrate side).
- Figure 4.** (a) Cross-sectional TEM images of the ZnO seeding layer on a Si(001) wafer with a 5 nm thick oxide layer in (a) overview with a SAED pattern from the crystallite labeled A and (b) higher-magnification of the crystallite A exhibiting a c-axis orientation with 0.52 nm (0001) ZnO lattice planes indexed.
- Figure 5.** Schematic of the ZnO NP's growth model: (a) the seeding polycrystalline layer formation at high Zn and O partial pressure; (b) the ZnO NP's growth on top of the c-oriented A-type crystallites via selective homoepitaxial growth at low Zn and O partial pressure; (c) the real SEM image of the ZnO NP's samples profile. The grains and NP's with their c-axis perpendicularly toward substrate surface are marked as $\uparrow C$, while for films it means the preferential texture; the parallel lines illustrate the parallel planes 00 l of ZnO.
- Figure 6.** Room temperature cathodoluminescence spectra of ZnO NP's, grown via selective homoepitaxial growth. The inset represents the respective panchromatic image of ZnO nanopillars luminescence (top view).
- Figure 7.** Low temperature (4 K) photoluminescence spectra of the ZnO nanopillars, grown via selective homoepitaxial growth at 500 °C (a) and the bulk ZnO crystal (b).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

a)

b)

c)

Figure 5.

Figure 6.

Figure 7.