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Effect of Ag doping on the microstructure and photoluminescence of ZnO nanostructures

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ZnO nanostructures were obtained by metal-organic chemical vapour deposition via Ag catalyst assisted growth in a temperature range of 200 – 500 °C. Growth at temperatures above 500 °C resulted in vertically aligned ZnO nanorods. Ag incorporation into ZnO up to 0.4 at. % promoted creation of basal plane stacking fault (BSF) defects and corrugation of the side facets of the nanorods. The presence of BSFs give rise to an additional photoluminescence peak with a wavelength of ~386 nm, which is slightly red-shifted compared to the commonly observed NBE emission at ~375 nm. The observed emission was found to be specifically observed from the side facets of the nanorods. It is suggested that this emission is due to a high concentration of BSFs in the ZnO as a result of an incorporation of Ag as acceptor dopant.

SEM image of an Ag-doped ZnO nanorod with corrugated side facets. The observed corrugation is accompanied by a high concentration of basal plane stacking faults.

1 Introduction ZnO is a promising semiconductor material for optoelectronics and photonics due to possible fabrication of highly efficient light emitting diodes (LEDs) and laser diodes (LDs) [1]. It possesses the largest family of nanostructures and once the location, shape and length-to-width ratio of the nanostructures can be controlled, it can be efficiently used in state-of-the-art bottom up semiconductor technologies. However, obtaining of ZnO with p-type conductivity, which is critical for most optoelectronic applications, is still posing a challenge and is practically unachievable [2]. One of the main obstacles is the self-compensation of ZnO as semiconductor, resulting in a high persistent electron concentration in the material ($\sim 10^{16} \text{ cm}^{-3}$), which is difficult to overcome by hole charge carriers. Earlier, group V elements have been suggested as acceptor dopants, but they create deep acceptor levels and the stability of the AX centre is a problem for As and P [3]. Group Ia elements tend to occupy the interstitial sites due to their small ionic radii, which limits their p-type doping capabilities [4]. Recent studies have been focused on group Ib, in particular Ag, for p-type doping [5, 6]. Ag, compared

to Cu and Au, has theoretically the most shallow acceptor level at only 0.3 eV above the valence band maximum [7]. Ag has the possibility to occupy two sites; Zn substitutional (Ag_{Zn}) and interstitial (Ag_{i}). The formation energy of Ag_{Zn} is lower than Ag_{i} , so Ag prefers to substitute Zn, which makes it an excellent candidate for p-type doping [8]. Finally, the radius of Ag^{2+} (0.089 nm) is only slightly larger than that of Zn^{2+} (0.074 nm), which may enable lower host lattice distortion in comparison to other acceptor dopants [9]. Maximum Ag solubility in ZnO is reported to be 0.76 mol. % at 1200 °C [10].

As a possible acceptor dopant in ZnO, Ag has a few additional advantages. Firstly, as a noble metal it can be used as a catalyst for growth of nanostructures via a vapour-liquid-solid process at rather low growth temperatures. Secondly, at increased Ag concentrations the dopant atoms may segregate into nanoscale Ag particles inside the ZnO matrix, which may provide exciton-plasmon coupling [11]. This can improve the internal light emission efficiency, which is beneficial for use in optoelectronics. However, as an impurity, Ag incorporation causes lattice distortion,

strain and stress, which degrades the light emission properties of the material.

In order to address these questions, we have studied Ag catalyst assisted growth of ZnO nanostructures in a low temperature range (200 - 550 °C) and investigated their microstructure and photoluminescence properties.

2 Experimental details

2.1 Sample preparation Si (100) substrates with a natural oxide were cleaned with RCI, TL1 and TL2 [12]. Then a thin layer of an organic suspension containing Ag particles (Ag paste) has been deposited on the substrate. The ZnO nanostructures were grown by atmospheric pressure metal-organic chemical vapour deposition (AP-MOCVD) with $\text{Zn}(\text{AcAc})_2$ from Sigma Aldrich as a precursor [13]. The precursor was loaded into an evaporator where the pressure was controlled via the evaporator temperature. The substrates were distanced from the evaporator and were located in the deposition zone. ZnO nanostructures were prepared at a constant precursor supersaturation with substrate temperatures in a range of 200 – 550 °C. All the substrates were simultaneously placed in the growth chamber, being subjected to the controlled temperature gradient in the growth zone. Ar gas was used as a carrier gas, with the flow rate 50 and 25 cm^3/min respectively. The total growth time was limited to 30 minutes. More details about the APMOCVD growth of ZnO nanostructures can be found elsewhere [12].

2.2 Characterisation The microstructure of the nanostructures was studied by scanning electron microscopy (SEM) using a Leo 1550 Gemini SEM operated at voltages ranging from 10 to 20 kV and using a standard aperture value of 30 μm . An elemental analysis of the samples was performed by ZEISS EVO 50 XVP SEM using energy dispersive X-ray spectroscopy (EDX) furnished INCA 450 (OXFORD Instruments). The operating voltage for EDX analysis was set to 20 kV. Microstructure study was carried out using conventional and high-resolution transmission electron microscopy (TEM). For cross-section transmission electron microscopy (XTEM) specimen preparation, two strips of the specimen were cut and glued face to face, and then they were mechanically thinned down to 25 μm . The specimens were subsequently thinned to electron transparency by Ar ion milling with an 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 a 0.194 nm point-to-point resolution was utilized. The photoluminescence (PL) from the ZnO nanostructures was investigated by micro-photoluminescence spectroscopy, carried out at 300 K with a continuous wave laser with a wavelength of 266 nm as an excitation source. The emitted luminescence was collected and mirrored into a single grating monochromator with a focal length of 550 mm and equipped with a 600 grooves/mm grating and a liquid nitrogen

cooled Si-CCD camera. The excited area was around 1-2 μm in diameter, providing an excitation density of 2 W/cm^2 .

3 Results and Discussions Fig. 1a-d presents the SEM images of ZnO nanostructures grown at 200, 300, 400 and 500 °C. Already at substrate temperature (T_s) as low as 200 °C, the ZnO deposits in an elongated shape, following the shape of the crystal grains, which is not peculiar for the growth of ZnO on a bare Si substrate at the same growth conditions [12]. This is attributed to that Ag particles available on the substrate surface provide nucleation centers for incoming ZnO material. The nanostructures do not possess hexagonal facets, as it is commonly observed, due to the tendency of ZnO to grow well faceted along the c-axis of its hexagonal structure [14]. Also, the mutual arrangement of the nanostructures is rather chaotic, reflecting absence of c-axis texture. We explain this as due to insufficient kinetic energy of Zn and O atoms for migration over the surface and occupying the most energetically favorable places. Thus, the incoming atoms are "frozen" on to the Ag provided nucleation sites. This is partially eliminated with further T_s increase (300 °C); the nanostructures start to be hexagonally faceted, and more vertically oriented due to improved c-axis texture.

Figure 1 SEM images of ZnO nanostructures of the samples grown at 200, 300, 400 and 500 °C (a, b, c, d respectively). The scale bar is 1 μm for all images.

The nanostructures grown at $T_s = 400$ °C are already well faceted and are all oriented with their c-axis perpendicular to the substrate plane. Furthermore, the grains are located close to each other, creating a "close packed" film. Thus, the microstructure of the nanostructures grown at 400 °C looks rather similar to that grown on a bare Si substrate with a low growth rate [12]. Additionally, sharpening of the nanostructures is observed, which is due to increased kinetic energy of the adatoms provided by the higher substrate temperature, and therefore increased ability of ZnO atoms to attach to the crystal plane with the lowest surface energy [15]. The situation changes signifi-

cantly for the nanostructures grown at 500 °C; the grains become textured, elongated and sharp. They are not that densely packed as the previous ones; the side facets of the grains are corrugated, while their tips are hexagonally sharply tapered. Further increase of T_s facilitates the observed features even more (Fig. 2a). Here the nanostructures can be divided into two types. Type 1 are the highly c-textured, grains of smaller diameter ~200 - 500 nm, which form the film at the bottom of the sample (Fig. 2b). Type 2 are longer and more bulky, highly faceted grains of average size ~1 - 1.8 μm , called nanorods (NRs). NRs possess highly corrugated side facets, and are also sharply hexagonally tapered. The NRs have an inverse sharpening structure: their diameter tends to increase with their height (Fig. 2c). Despite the size, the nanostructures of both types are similar and possess highly corrugated side facets. Presumably, large NRs are a result of kinetically driven heterogeneous nucleation processes on the Si surface. The early nucleated cluster had a chance to grow faster and, being vertically oriented, was shadowing the other nanorods. Therefore, the diameters of the NRs are increasing with their height. The details of the morphology of the ZnO nanostructures are summarized in Table 1.

Figure 2 SEM images of ZnO nanostructures, grown at 550 °C: a) top view of the sample b) top view of the smaller grains of type 1; c) cross-section of the NRs type 2. The scale bar is 10 μm for a) and 1 μm for b) and c).

The effect of side facet corrugation is an interesting phenomenon and need to be clarified. Usually, ZnO nanostructures grown at normal conditions by CVD or carbon thermal reduction (CTR) has flat and uniform side facets, independently of the substrates [14, 16]. Glushenkov et al. has reported the only former case of pure ZnO nanostructures with unusual corrugated side facets [17].

Table 1 Details of the microstructure and the morphology of the ZnO nanostructures, grown at temperatures in the range 200 - 500 °C.

T_s , °C	Shape	Texture	Size
200	Blunt tapered rods	No texture	Rods of diameter $0.5 \div 1 \mu\text{m}$
300	Blunt tapered rods, slightly sharpened at the end	Some c-texture appears	Rods of diameter $0.5 \div 0.8 \mu\text{m}$
400	Densely packed	Strong c-axis	Grains of di-

	grains with hexagonal faceting	texture	ameter $0.5 \div 0.8 \mu\text{m}$
500	Densely packed hexagonally faceted grains with corrugated surface	Strong c-axis texture	Grains of diameter $0.2 \div 0.5 \mu\text{m}$
550	Two types of grains: 1 – densely packed hexagonally faceted 2 – bulk and long NRs with inverse sharpening	Strong c-axis texture for type 1.	Type 1: $0.2 \div 0.5 \mu\text{m}$ Type 2: $1.0 \div 1.8 \mu\text{m}$

It was concluded that the side surface corrugation is a result of high concentration of basal plane stacking faults (BSFs) in the material. Their appearance is attributed to the high supersaturation during the growth. Meanwhile corrugation of the side facets was numerically observed for nanostructures of ZnO, doped with acceptor dopants. Recently Park et al. [18] reported on Sb doped ZnO nanostructures. Interestingly, the surface corrugation was only observed in the areas of the nanostructures where the Sb was introduced.

Figure 3 a) TEM image of the cross-section of the Si/Ag/ZnO interface of the NRs sample, grown at 550 °C; inset is a selected area electron diffraction image of the hexagonal ZnO crystal structure. Ag concentration in the tip of the NRs ~3.79 at. % (b) and inside of the NR ~0.42 at. % (c), measured by EDX analysis. The scale bar is 200 nm in a) and 40 nm in b) and c).

Taking into account the large differences in the ionic radii of 0.074 nm for Zn and 0.245 nm for Sb, it is expected that incorporation of Sb into ZnO is accommodated by the creation of extended defects such as stacking faults (SFs) and dislocations.

According to Glushenkov et al. corrugation of the side surfaces of nanostructures is attributed to high SF concentration. Thus, the side facets corrugation may be attributed to acceptor, Sb or Ag, incorporation. Since in our case the most corrugated side facets were observed for the NRs, we have studied them in detail. We have studied the distribution of Ag atoms in the NR samples. EDX analysis of the cross-section of the Si/Ag/ZnO sample performed by TEM,

demonstrated small particles of Ag with a lateral size around 20 nm on the Si/ZnO interface (Fig. 3).

Figure 4 a) TEM image of the ZnO/Ag/Si interface: the rhombohedral particles of Ag are visible; the scale bar is 100 nm. The area marked in green is used for the EDX analysis, and the distribution of Ag inside the ZnO matrix is shown in (b).

Thus, we can conclude that Ag partially stays at the Si/ZnO interface even for the samples grown at 550 °C. Figure 3 shows the Ag nanoparticles of size ~30 nm, located on the Si/ZnO interface. This, however, does not exclude that Ag is partially incorporated into ZnO. We have studied the Ag content inside the NRs by EDX spectroscopy in two specific locations: inside the NRs and on its top (Fig. 3c and d). The Ag content on the top of the NR was found to be 3.8 at. % in comparison to 0.4 at. % inside of the NR. The atomic distribution of Ag near the interface is depicted in Fig. 4.

A TEM study of the cross-section of ZnO/Ag/Si has revealed additional unusual contrast in bright field mode. The featured lines were located parallel to the substrate plane, e.g. perpendicular to the c-axis of the NR. Presuming that the reason for this is the extended defects, we have studied individual NRs by high resolution TEM. A number of basal plane [0001] stacking faults were observed, penetrating the NRs perpendicular to its c-axis (Fig. 5). BSFs were found to be quasiperiodically inserted every 5 - 10 nm along the NRs. It has to be mentioned that SFs are observed in both types of NRs. We attribute the appearance of BSFs as due to the Ag dopants. Earlier, it has been shown that Mg as an acceptor promotes the formation of SFs in GaN [19]. We believe that the same scenario can be applied in our case; Ag, having a rather different radius than Zn, when incorporated into ZnO provides local strain, which favours SF formation. At present it is not clear exactly where the Ag atoms are located; i.e. in the proximity of SFs or not, which has to be studied in the future.

Figure 5 High resolution TEM image of ZnO NRs. The SFs are shown by arrows. The scale bar is 5 nm.

SF may be of three types: i) basal plane SF, ii) prismatic SF, and iii) partial dislocations-terminating basal-plane SF. Among them, basal plane stacking faults (BSF) are the most common type of SFs (~90%) in wurtzite materials. Availability of SFs can modify the optical properties of the material. It was recently demonstrated, that SFs in wurtzite-structure (WZ) ZnO, can be considered as a minimal segment of zinc blende structure (ZB) embedded in the parent crystal [20]. Due to the smaller band gap of the ZB modification, these SFs can form perfect ZB-like quantum wells (QWs) in a WZ matrix. Thus, the optical properties of ZnO with a lot of SFs can be significantly modified. However, ZnO SF are difficult to be identified in PL spectra, since the spectral location of the SF peak (3.314 - 3.333 eV) overlaps with peaks from acceptor bound exciton recombination or two electron satellites (TES) of the dominating D⁰X peak.

We have studied micro-PL spectra of ZnO:Ag NRs at RT by mapping the surface of the sample and probing both types of NRs (Fig. 6). It has to be noticed that the excitation laser beam was directed perpendicular to the substrate plane. Thus, both types of NRs were probed. Earlier, we suggested that the growth/formation mechanism of both NRs is identical and the only difference is their size. While the difference in their PL spectra is due to their different arrangement and thus, different areas irradiated. Smaller nanorods of type 1 are vertically oriented and therefore only their top parts are irradiated (position 1 on Fig. 6). Due to a rather shallow penetration depth of the ultraviolet laser, only a small part of the BSFs are excited. Therefore, the NBE emission at ~375 nm is strongly dominating with a small tail, evidencing that emission at ~386 nm is existing. However, the tail grows as the laser excitation area is

moved toward the NRs of type 2 (positions 2-6). Finally, when only the NRs of type 2 are irradiated, both peaks are present on the PL spectrum (position 7).

In other words, while NRs of type 1 were excited from the top, some of the NRs of type 2 were tilted or located with their c-axis parallel to the substrate plane. Thus, their side facets were in fact excited by the laser beam. As one can see, top excitation of the NRs results in a regular ZnO luminescence with one peak at ~ 375 nm (~ 3.31 eV). This is commonly observed near band edge excitonic emission in ZnO [21]. However, once the facets of the NRs were probed, an additional peak appears in the PL spectrum on the low energy side of the previously mentioned peak. The new PL gains its maximum intensity when the side facets of NRs of type 2 are under maximum irradiation and peaks at ~ 386 nm (~ 3.21 eV), while the previously mentioned NBE peak still being visible at 375 nm.

Figure 6 Micro-photoluminescence spectra of luminescence from different positions of the ZnO:Ag NRs sample. The mapped area is shown in the inset. The mapping positions are marked in red. The scale bar in the inset is 500 nm. Spectrum assigned as position 1 is obtained by excitation of the top planes of ZnO NRs. Positions 2-6 correspond to excitation of areas of both top and side planes of NRs. Position 7 corresponds to excitation of only the side facets of a NR.

The peak at ~ 386 nm appears because when we excite the NRs of type 2, mostly the side facets are illuminated, thus a large number of emanating SFs are excited, which contribute to the intense PL peak ~ 386 nm. We have noticed that for all other samples, grown at $200 - 400$ °C, only a PL peak at 375 nm is observed (not shown here). This implies that the appearance of the peak at ~ 386 nm is attributed to the availability of both Ag and SFs. The nature of the PL may be explained as an indirect exciton recombination from an electron localized in the QW in the conduction band of zinc blende ZnO with a hole localized near an acceptor in the proximity of a SF in wurtzite ZnO, as it has been observed in Mg doped GaN [19]. However, a de-

tailed study is necessary to clarify this recombination scheme in the ZnO NRs.

4 Conclusions To summarise, we have studied doping of ZnO by Ag at temperatures as low as 500 °C. It has been demonstrated that Ag affects the growth by creating additional nucleation centres, favouring the growth of nanostructures. During growth at substrate temperatures above 500 °C, Ag incorporates into the ZnO lattice, as well as is partially staying on the Si/ZnO interface. NRs grown at substrate temperatures of 500 °C and above have corrugated side facets, which is attributed to the appearance of basal plane stacking faults (BSF). Their appearance is suggested to originate from Ag incorporation (~ 0.4 at. %) into the ZnO NRs. Availability of BSFs affects the PL spectrum of the ZnO NRs by providing an additional peak at ~ 386 nm. The peak is attributed to BSFs. The PL due to SFs is mostly observed from the side facets of the NRs. This may be useful in terms of explaining the PL properties of non-polar grown ZnO films, in which the possible SFs can be optically active and produce a similar PL signal.

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