



# Photoluminescence study of ZnO structures grown by aqueous chemical growth

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## ABSTRACT

ZnO micro-structures were deposited by aqueous chemical growth on Si (100) substrates, their morphology and size depending on the growth period. Characterization of the structures was performed using X-ray diffraction, scanning electron microscopy and Raman spectroscopy. Photoluminescence spectra recorded at 18 and 295 K for 325 nm CW excitation indicated that these are strongly affected by the morphology of the structures. Rods and tubes emit stronger UV radiation, in contrast to stronger yellow-green emission observed for flower-like structures. A red shift of the UV emission was found for increasing input power, while, thermal annealing of the samples induced stimulated emission for quite high excitation intensities.

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## 1. Introduction

Nanostructured materials are expected to exhibit improved optical properties as compared with bulk materials due to their large surface area to volume ratios, size effects and possible quantum confinement effects, their optical response strongly depending on their size, shape and environment [1]. As a result, the growth of nanostructures of various sizes and morphology has attracted a lot of interest since these can be suitable for the fabrication of nanoscaled electronic and optoelectronic devices [2]. Among others, ZnO is a II–VI compound semiconductor with a wide and direct band gap of approximately 3.37 eV and large exciton binding energy (60 meV), being therefore useful for optoelectronic applications [3,4]. As an example, ZnO structures have been extensively investigated as short-wavelength light-emitting devices, possibly suitable for the replacement of GaN [4,5].

Various chemical and physical methods have been applied for the growth of the ZnO nanostructures [6–10]. As a result, one-dimensional ZnO nanostructures such as nanorods, nanowires and nanotubes, nanoneedles and nanobelts as well as two- and three-dimensional structures including nanosheets, nanoribbons, nanoflowers, nanocombs and nanosaws have been successfully synthesized and studied. Regarding their photoluminescence characteristics, it has been demonstrated that these are significantly affected by the morphology of the grown structures [10–13]. As a general observation,

in all photoluminescence spectra recorded for ZnO nanostructures, two bands could be clearly seen, one in the UV and one in the visible spectral regions, their relative intensity depended on the structures' size and shape [11,12].

Compared with other methods, aqueous chemical growth (ACG) is a simple, low cost technique allowing the synthesis of advanced nano-, meso-, and micro-particulate thin films at mild temperatures (below 100 °C), using non-toxic reagents and producing non-hazardous by-products. Employing ACG, the morphological and structural characteristics of the grown structures can be normally controlled via the concentration of solution, the reagents molar ratio, the substrate, the temperature and the growth time [14,15].

In this work, we performed a parametric study regarding the capability of controlling the emission characteristics of ZnO micro-structures through their morphology, which strongly correlates with deposition time. For this study, the simple and low cost aqueous chemical growth technique was employed, allowing the control of the structures' morphology by varying the growth conditions at temperature as low as 95 °C.

## 2. Experimental

ZnO structures were grown by the aqueous chemical growth (ACG) technique on Si (100) substrates using equimolar (0.01 M) aqueous solutions of zinc nitrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) as precursors. Before deposition, the substrates were first cleaned with spectroscopic grade propanol and acetone, washed with MilliQ water (where MilliQ refers to water that has been purified and deionized to a high degree by a water purification system manufactured by Millipore Corporation) and dried

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under  $N_2$  gas flow. The substrates were then placed in Pyrex glass bottles with polypropylene autoclavable screw caps, containing the precursor described above, and heated at 95 °C for several hours [15]. After growth, the substrates were thoroughly washed with the same water to eliminate residual salts or amino complex, and dried in air at the same temperature.

The crystal structure of the ZnO structures was determined by XRD, using a Rigaku (RINT 2000) diffractometer with Cu  $K\alpha$  X-rays, and Raman, employing a T-64000 model of Jobin Yvon (ISA – Horiba group) at an excitation of 514.5 nm. In addition, the surface morphology was examined by SEM using a JEOL JSM-840 electron microscope. The photoluminescence measurements were carried out using a He–Cd CW laser at 325 nm with full power 35 mW as the excitation source, from 18 K to room temperature. The spectra were recorded using a LN2 cooled CCD camera and spectrometer with UV blazed grating.

### 3. Results and discussion

ZnO micro-structures were deposited on Si (100) substrates using ACG, for various growth times ranging from 1 up to 72 h, the morphological and crystal properties of samples grown for periods up to 40 h discussed in details elsewhere [15]. Briefly, all structures grown for 1–40 h were found exhibiting sharp XRD peaks characteristic of the ZnO wurtzite hexagonal phase, an observation demonstrating the growth of pure ZnO only [15]. The fine crystalline quality of the grown samples was indicated by the full-width at half-maximum (FWHM) of the (100) diffraction peak, which was found optimum for a deposition period of 15 h, being around 0.1595°. For longer deposition times, the crystallinity of the structures was found reducing, the corresponding full-width at half-maximum (FWHM) of the (100) diffraction peak approaching a value of 0.1692°, for the 40 h growth. Regarding the SEM results, these showed that for growth times up to 30 h, rods are mainly grown, all having hexagonal cross section, also implying the occurrence of the wurtzite hexagonal ZnO crystal structure. With increasing growth time, the structures were becoming gradually larger. For 1 h growth, the diameter and the length of the rods were around 500 nm and 5  $\mu\text{m}$  respectively, becoming 750 nm and 10  $\mu\text{m}$  for longer growth periods (30 h). For deposition times of around 40 h, flower-like structures are grown, consisting of rods having length and diameter of about 12 and 1  $\mu\text{m}$  respectively. Regarding the 72 h grown samples, these were exhibiting lower crystalline quality. As shown in Fig. 1, the XRD pattern for a 72 h sample was quite noisy and some extra XRD peaks (indicated with an asterisk) were present, as compared to the spectrum recorded for a 15 h sample (spectrum representative for samples grown for periods shorter than 40 h). These peaks could be attributed to Zn(OH)<sub>2</sub>, an assumption also verified by the Raman spectra shown in Fig. 1. Comparing the Raman spectra of samples grown for 15 and 72 h, the peaks were blue shifted in the latter case, a behavior indicating oxygen deficiency. Moreover, two extra bands were recorded for the 72 h sample, at 352  $\text{cm}^{-1}$  (translational mode) and 822  $\text{cm}^{-1}$  ( $R_{\text{OH}}$ ), bands that can be attributed to Zn(OH)<sub>2</sub>. Regarding the morphology of the 72 h samples, this was found quite different, since brushes and hexagonal shaped tubes were clearly observed, a behavior that may be due to the co-existence of ZnO and Zn(OH)<sub>2</sub>, as indicated by XRD and Raman. Regarding the coverage of the substrate, this was found increasing from 40% up to 85% as the growth time was increased from 1 to 30 h, remaining approximately constant for longer growth times.

Photoluminescence (PL) spectra of the ZnO micro-structures grown on Si substrates were recorded at 18 K (LT) and room temperature (RT) in the wavelength range from 350 to 650 nm, using 325 nm CW radiation as the excitation source. In all recorded spectra, two main broad emissions were indeed observed in the UV and the visible spectral regions respectively, their intensity and shape

depending on the growth time of the ZnO structures. Fig. 2 presents these two characteristic PL emission bands, for typical ZnO rods grown on Si (100) for 30 h. The excitation radiation intensity was kept low enough so that no saturation effects are present. For the growth conditions used, the UV emission was found slightly stronger than the visible one for the LT case, the opposite appearing in the RT spectra. Moreover, both UV and visible emission bands were found shifted for RT emission.

The UV emission is known to originate from excitonic recombination corresponding to the near band gap emission [4,16]. In our case, the UV emission at LT clearly exhibits two bands; a strong one peaked at around 3.321 eV, the band attributed to bound excitons, and a weaker one near 3.356 eV ( $35 \pm 1$  meV higher than the bound exciton band), which can be attributed to free excitons. The position of the maxima of these bands was shifted, depending on the morphology of the structures, the observed shift however being within the error limits (<1 meV). Moreover, two shoulders were also present (not clearly seen in all recorded spectra), centered at around 3.251 and 3.182 eV, their separation from the bound exciton peak being 70 meV and 139 meV respectively. Therefore, taking into account that the theoretical value for the ZnO longitudinal optical (LO) phonon replica energy is around 72 meV, these shoulders can be attributed to the first- and second-order LO phonon replicas of bound exciton. The position of the maxima of the UV bands was shifted, depending on the morphology of the structures, the observed shift however being around the error limits (1 meV). Similar bands in the low temperature PL of ZnO structures have been reported by various groups [17–19], the position of their peaks depending on the growth conditions and the morphology of the structures.

Regarding the broad visible emission, it is known that, in addition to UV excitonic emission, ZnO structures frequently exhibit visible luminescence at different wavelengths in the green, yellow and orange band of the spectrum, an emission usually attributed to intrinsic or extrinsic defects [4,13,17]. Several mechanisms have been proposed to explain the emission of the visible photoluminescence from ZnO structures, its origin, especially for the green emission, still being controversial. As an example, various mechanisms have been proposed to explain the green emission (at around 2.3 eV), such as transition between singly ionized oxygen vacancy and photoexcited hole, transition between electron close to the conduction band and a deeply trapped hole at  $\text{Vo}^{++}$ , surface defects etc. [13]. Moreover, the yellow–orange defect emission observed in ZnO is typically assigned to interstitial oxygen, dislocation related luminescence centers and Li dopants [13]. Green emission is therefore in general associated with oxygen deficiency, while yellow/orange emission (at around 2.1 eV) with excess oxygen. The visible emission observed in our case (Fig. 1) seems to consist of four discrete bands, centered at 2.093, 2.161, 2.204 and 2.268 eV respectively. Therefore, the yellow emission dominates our spectra, a behavior indicating excess oxygen, which however was not possible to be recorded with the characterization techniques available.

As far as it concerns the ratio R between the integrated intensity of the UV and the visible emissions, this has been reported to correlate with the radius of grown nanowires [11], but also found to depend on their morphology [12]. For the ZnO structures grown in our case at 95 °C, it was found that the ratio depends on the growth time, the dependence correlating with the morphology of the structures. An example of this correlation is shown in Fig. 3, which presents SEM images of ZnO structures grown on Si for (a) 20, (b) 40 and (c) 72 h and the corresponding PL spectra, recorded at LT using CW laser excitation. As shown, 20 h growth results in rods having 10–12  $\mu\text{m}$  length and 1–1.5  $\mu\text{m}$  diameter, structures exhibiting UV emission stronger than the visible one, the corresponding ratio R approaching a value of 1.65. On the other hand, flower-like structures grown for 40 h, consisting of rods having 12  $\mu\text{m}$  length and 1  $\mu\text{m}$  diameter, were emitting stronger in the visible, with an R value of 0.63. Finally, tubes

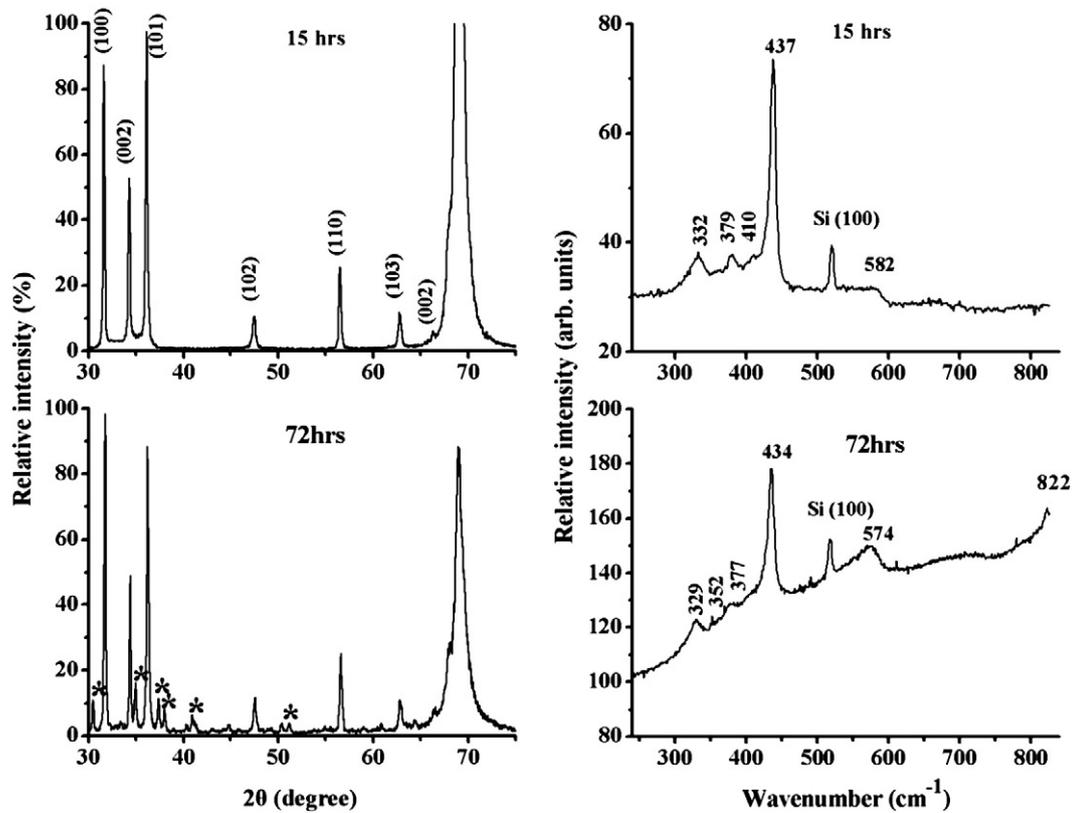


Fig. 1. XRD (left) and Raman (right) spectra for the samples grown for 15 and 72 h respectively.

of 8  $\mu\text{m}$  length and 750 nm outer diameter grown for a period of 72 h, resulted in an R value of 7.4, therefore, quite strong UV emission. Regarding the strong UV emission observed for 72 h growth, this cannot be attributed to other properties like better crystallinity, since, as was found in the XRD analysis, for growth periods longer than 15 h, the crystallinity of the ZnO structures is reduced. Therefore, the strong UV emission observed in the case of the 72 h growth can be attributed only to the presence of either hexagonal shaped ZnO tubes or Zn(OH)<sub>2</sub>, as indicated by the SEM and the XRD results.

Moreover, regarding the influence of the rod diameter on the ratio R [11], this seems to be in general valid. As an example, for 20 h growth (Fig. 3a), a ratio of 1.65 was determined for a rod diameter of around 1–1.5  $\mu\text{m}$ . When the growth time was increased to 30 h (Fig. 2), the diameter of the rods was reduced to 0.75–1  $\mu\text{m}$ , resulting in a ratio of about 1.42. However, increasing growth time resulted in a simultaneous modification of both the dimensions and the shape of

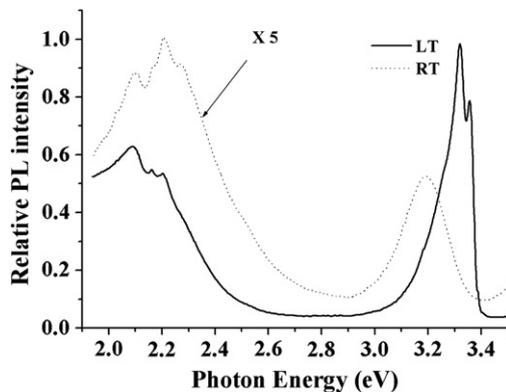
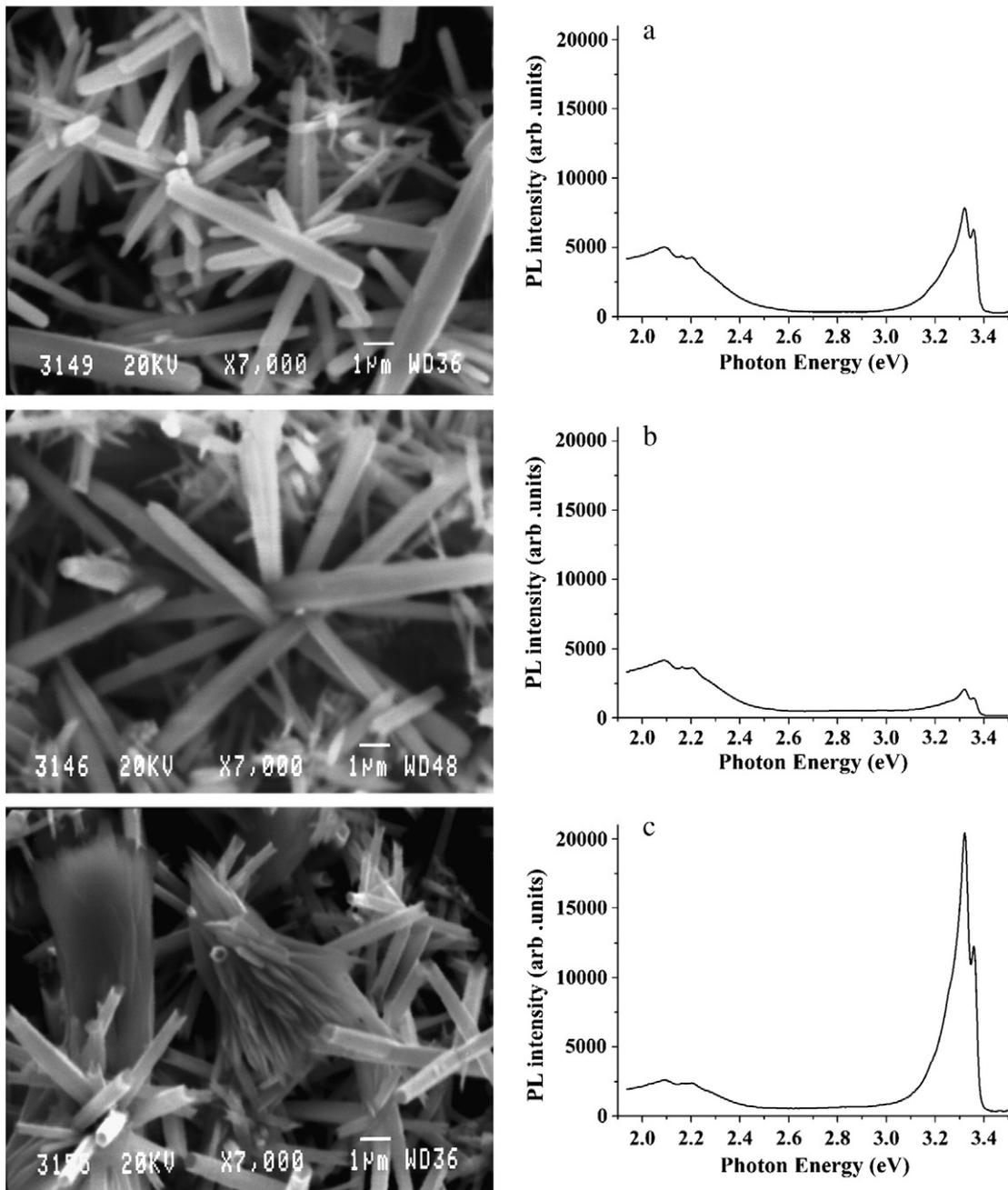


Fig. 2. Low and room temperature CW photoluminescence bands of typical ZnO rods grown on Si for 30 h.

the structures, a behavior not allowing a clear picture of the individual influence of each morphological parameter on the PL emission. In any case, as a general conclusion one can say that the low temperature PL emission spectra characteristics are strongly affected by the morphology of the grown structures. Further investigations are under way in order to better understand the growth and the emission mechanisms as well as the influence of the growth parameters like solution concentration, temperature and substrate on the properties of the grown structures.

Regarding the RT spectra, these were also found to consist of UV and visible emission bands. However, increasing temperature was found to induce a significant red shift in the UV bands, the resulted spectrum consisting of one band only. Similar behavior has been reported by several groups [18–20] and can be attributed to the decomposition of bound excitons to free excitons at room temperature, which results in the emission from free exciton only. The position of the UV peak for RT emission was found to depend on the growth time, therefore, correlating with the morphology of the grown structures. For short (rods) and long (tubes) growth times, the peak of the UV band was around 3.195 eV, while for growth times around 40 h (flower-like structures), the peak was found shifted to 3.035 eV. Moreover, the UV band was observed to be always weaker than the visible one, their ratio also depending on the growth time. However, the overall response was opposite than that for LT spectra, since maximum ratio R was obtained for flower-like structures.

The dependence of the photoluminescence of the grown ZnO structures on the intensity of the excitation radiation was also examined. As was observed, the peak of the UV bands was red shifted with increasing input power, the peaks of the yellow–green bands remaining unaffected. Fig. 4 presents the shift of the two UV peaks as a function of the input power, for ZnO structures grown on Si for 20 and 72 h respectively. As can be seen, longer red shifts are induced for the 20 h growth and the free exciton band. Regarding the yellow–green emission, no shift was observed with increasing input power, at least



**Fig. 3.** Low temperature CW photoluminescence spectrum of ZnO structures and the corresponding SEM images of: (a) rods corresponding to 20 h growth, (b) flowers corresponding to 40 h growth and (c) tubes corresponding to 72 h growth, all deposited on Si.

for the range of powers used. The red shift of the UV peaks with increasing input power can be attributed to electron–phonon interaction at elevated temperatures, which can be induced by laser heating [21]. Finally, a similar response was recorded for structures grown for other time periods.

Regarding the dependence of the emitted intensity  $I$  on the laser excitation power  $P$  ( $I \sim P^k$ ), this was found more or less similar for all emission bands and structures grown for different deposition periods. For low enough input power, both bound and free exciton UV emission bands were found increasing nearly linear, exhibiting an exponent factor (slope of the curve) around 1.1. With increasing input power, saturation appeared in both bands, reducing the exponent value down to 0.6. Due to the observed saturation, the previous analysis of the photoluminescence of the grown ZnO structures was performed on spectra recorded for input powers lower enough to

avoid saturation. For the case of the yellow–green bands, the dependence was found similar, the corresponding exponent factors being slightly smaller, approximately 1.06 and 0.4 below and above saturation respectively. Similar behavior was found for structures grown for different time periods, all exponent factors being in the range 1.04 up to 1.25, the variation depending on the morphology of the grown structures.

Previous studies [22–24] have shown that the dependence of the emitted intensity on the laser excitation power  $P$  is in general related to the mechanism involved. For a near-band-edge PL emission, the exponent factor  $k$  has been reported to be larger than 1 for exciton-like transitions, while for free-to-bound and donor–acceptor pair transitions the  $k$  values were less than 1 [22,23]. As a result, the nature of the UV emission of different ZnO structures could be identified in some cases [25]. However, in other cases, the exponent  $k$  appeared not

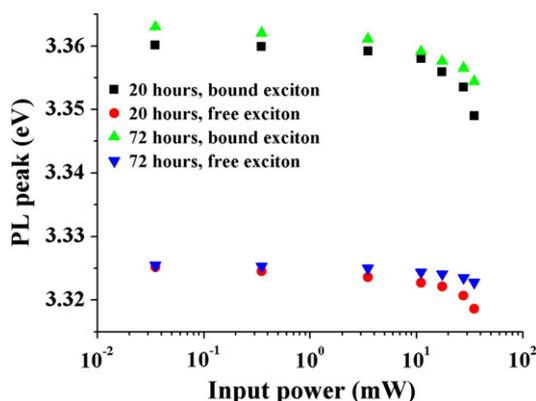


Fig. 4. Shift of the UV peaks as a function of the input power for rods grown for 20 h and tubes grown for 72 h.

to be an appropriate rule for the distinguishing of the different origin of the UV emission in ZnO structures, since various effects present in the light–matter interactions can affect the emission process [24]. This seems to apply in our case, where similar dependence was recorded for all growth times.

A rather interesting behavior in the intensity dependence of the photoluminescence was recorded when thermal annealing in air was performed on the structures grown for 72 h, structures exhibiting the strongest UV emission. As can be seen in Fig. 5, ZnO structures grown on Si for 72 h and annealed at 100 °C for 30 min exhibit a vast increase of the emitted UV intensity for CW powers higher than 28 mW, the corresponding exponent factor approaching 8. This behavior indicates that after annealing, our ZnO structures possibly exhibit stimulated emission, a response that can be suitable for laser action. Both bound and free exciton emission present this behavior, the corresponding yellow–green bands exhibiting always normal intensity dependence. This behavior can be attributed to the increased presence of Zn(OH)<sub>2</sub>, as indicated by the increased intensity of the corresponding XRD peaks.

#### 4. Conclusions

The low and room temperature photoluminescence of ZnO structures grown on Si substrates by ACG for various time periods was examined for CW laser excitation. In all cases, emission was recorded in both the UV and yellow–green spectral regions, their relative intensity depended on the morphology of the structures, morphology strongly correlating with the growth time. More specific, rods and tubes were found to emit stronger UV radiation, in contrast to the stronger yellow–green emission observed for flower-like structures. Increasing input power was found to induce a red shift of the UV emission, the yellow–green emission remaining unaffected. Thermal annealing of the structure was observed to induce the appearance of stimulated emission for quite high excitation intensities.

Therefore, using a simple, low cost growth technique, requiring non-toxic reagents and producing non-hazardous by-products, one can synthesize advanced ZnO micro-structures suitable for light optoelectronic devices emitting in both the UV and the yellow–green spectral regions, the emission characteristics depending on the morphology and the size of the structures. Moreover, the employment

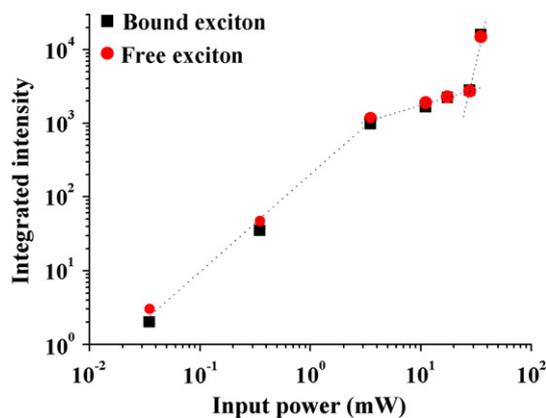


Fig. 5. Intensity dependence of UV photoluminescence for annealed ZnO samples grown for 72 h.

of annealing can result in ZnO structures exhibiting strong stimulated emission, a property which may find applications in laser technology.

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