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# Morphological and optical studies of self-forming ZnO nanocolumn and nanocone arrays grown by PLD on various substrates

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ZnO nanostructures were grown by pulsed laser deposition on c-sapphire, Si (111) (n-type and p-type) and analysed using morphological and optical techniques. Under optimized growth conditions, self-forming arrays of vertically aligned nanostructures were obtained. Scanning electron microscopy studies revealed two main structures: nanocolumns and a ‘moth-eye type’ array of nanocones, which gave a graded effective refractive index. X-ray diffraction measurements indicate that both types of structures are highly oriented along the *c*-axis. The optical properties were investigated using low temperature photoluminescence (PL) and room temperature (RT) reflection measurements. Low temperature PL spectra for nanocolumns

grown on sapphire and n-type Si showed an emission which is similar to that observed for bulk ZnO with a spectrum dominated by donor bound exciton recombination at ~3.36 eV and a structured green band. The PL intensity was particularly enhanced for nanocone structures grown on cubic Si substrates. For these samples, additional features, which are not observed for bulk ZnO were observed at 3.12, 3.02 and 2.92 eV following a vibronic progression of 100 meV. RT angular-dependent specular reflection measurements indicated that all the nanostructures act as highly effective broadband antireflection coatings.

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**1 Introduction** During the last decade, zinc oxide nanostructures have been extensively studied due to their potential relevance in optoelectronics, spintronics and bio-applications [1]. Pulsed laser deposition (PLD) is recognized as one of the most powerful techniques for the growth of ZnO-based thin films and it has recently shown a tendency for the growth of self-organizing ZnO-based nanostructures arrays [1–3]. In previous studies [4], it was found that self-forming arrays of vertically aligned nanocolumns and nanocones can be grown by PLD under optimized growth conditions. It was proposed that such arrays of nanostructures could be useful for enhancing light extraction and/or absorption in optical devices. Indeed, simple p–n heterojunction LEDs made with such n-type ZnO nanocone arrays grown on p-type Si were found to give rectifying characteristics and blueish–white electroluminescence which was visible to the naked eye [5].

The purpose of the present work is to examine the morphological and optical properties of these PLD grown ZnO nanostructure arrays by scanning electron microscopy (SEM), photoluminescence (PL) and angle resolved reflectivity (ARS). The sample optical properties will then be discussed and correlated with their morphological and structural properties.

**2 Experimental** Substrates of Si (111) and c-plane sapphire (c-Al<sub>2</sub>O<sub>3</sub>) were used for the growth of the ZnO nanostructures. The samples were grown by PLD from a 99.99% pure ZnO target using a KrF excimer laser (248 nm) as described elsewhere [3–5]. The sample morphology was studied using a Hitachi S4800 field emission-SEM.

X-ray diffraction (XRD) was carried out in a Panalytical MRD Pro system in order to investigate the crystal structure of the samples.

Optical properties were assessed by PL and reflection. For the PL measurements, the samples were mounted on a cold finger in a continuous flow cryostat permitting temperature control in 14 K to room temperature (RT) range. A He–Cd laser ( $0.6 \text{ W/cm}^2$ ) was used as the excitation source. The sample emission was dispersed using a SPEX1704 spectrometer and detected using a cooled photomultiplier. RT reflection measurements were performed using an Ocean Optics UBS4000 spectrometer and computer-controlled rotation stages. The sample was illuminated with a collimated beam of a tungsten/halogen lamp. The rotation stages and the spectra acquisition were piloted with home-made software.

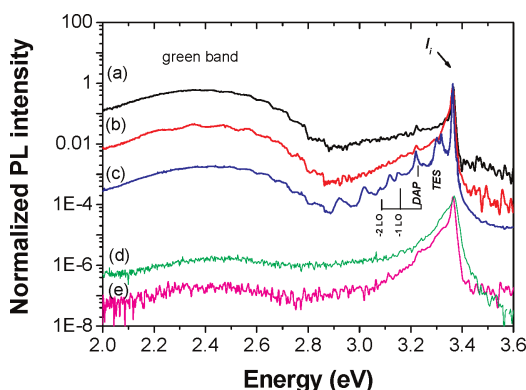
**3 Results and discussion** Figure 1 shows typical SEM images of the two kinds of nanostructure arrays observed in the samples. Figure 1(a) reveals nanocolumns of rather uniform shape, aligned preferentially along the perpendicular to the Si (111) substrate plane. They are averaged 200 nm in diameter and about  $3 \mu\text{m}$  in length. Figure 1(b) shows the ‘moth-eye’ type array of nanocones, which was obtained on the same substrate by changing the growth conditions [4, 5]. The nanocones are also aligned preferentially along the perpendicular to the substrate plane and are typically  $3 \mu\text{m}$  in length with an average diameter of about 200 nm at the base.

Five samples were selected for studies: nanocolumns/ $c\text{-Al}_2\text{O}_3$ , nanocolumns/n-Si (111), nanocones/ $c\text{-Al}_2\text{O}_3$ , nanocones/n-Si (111) and nanocones/p-Si (111).

XRD measurements indicated that all the samples had single-phase wurtzite structure with  $c$ -axis highly oriented along the growth direction, as discussed elsewhere [4, 5].

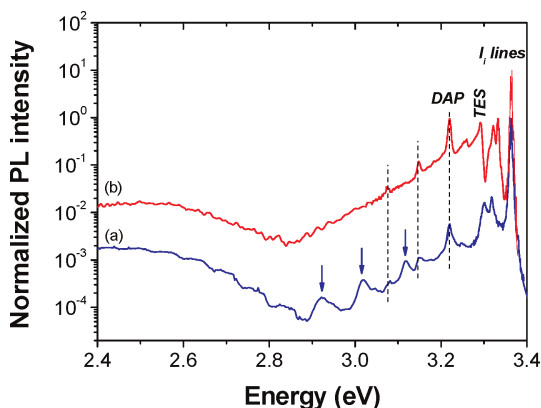
Low temperature PL spectra of the analysed samples are shown in Fig. 2.

Besides the ultraviolet recombination due to free and bound-excitons ( $I_i$  lines) and the donor–acceptor pair transitions (DAP) [6–8] the structured and unstructured green-emission band [9, 10] is also present in these samples, as is observed for some ZnO bulk samples. A closer inspection of the PL spectrum for the ZnO nanocones/n-Si

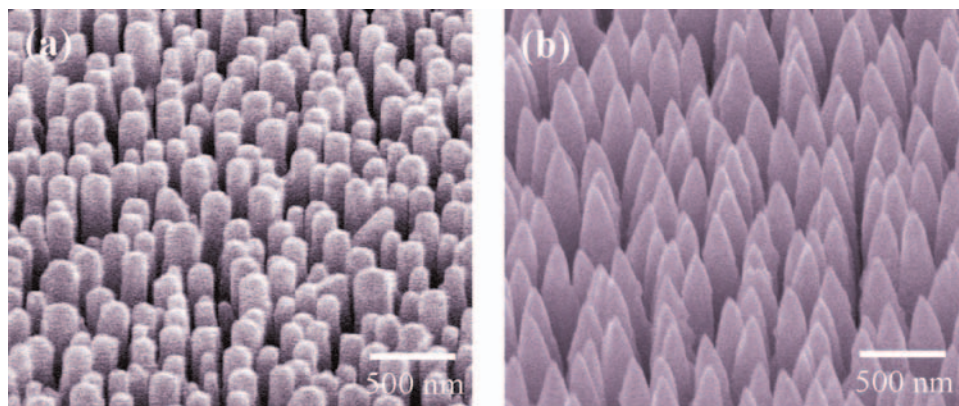


**Figure 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) 14 K PL spectra of the PLD grown ZnO (a) nanocolumns/ $c$ -sapphire, (b) nanocolumns/n-Si(111), (c) nanocones/n-Si (111), (d) nanocones/p-Si (111) and (e) nanocones/ $c$ -sapphire. The (d) and (e) spectra were vertically shifted.

(111) sample reveals additional features to the ones observed in bulk samples as indicated by arrows in Fig. 3. The lines at 2.92, 3.02 and 3.12 eV have a constant energy separation of 100 meV, suggesting a vibronic progression. The same



**Figure 3** (online colour at: [www.pss-b.com](http://www.pss-b.com)) 14 K PL spectra of the (a) PLD grown ZnO nanocones/n-Si (111) and (b) a typical bulk ZnO sample.



**Figure 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) SEM images of the two kinds of morphologies observed in samples: (a) ZnO nanocolumns/n-Si (111) and (b) ZnO nanocones/n-Si(111).



features were not detected in the PL spectra of the other PLD grown nanostructures suggesting an additional optical active defect in this sample.

To investigate the characteristics of the ZnO ‘moth-eye’ nanostructures [5], antireflection RT specular reflection measurements were performed as a function of wavelength in the range 450–720 nm and for angles of incidence between 10 and 60°. Figure 4 shows the RT reflection of the (a) nanocolumns/n-Si (111), (b) nanocones/n-Si (111) and (c) nanocones/p-Si (111), normalized to the reflection from the silicon substrate reference. As observed in Fig. 4(b) for the ZnO nanocones/n-Si a periodic pattern was found which is likely due to an unwanted oxide layer or related to

morphological aspects (length and tapering of the nanorods tips).

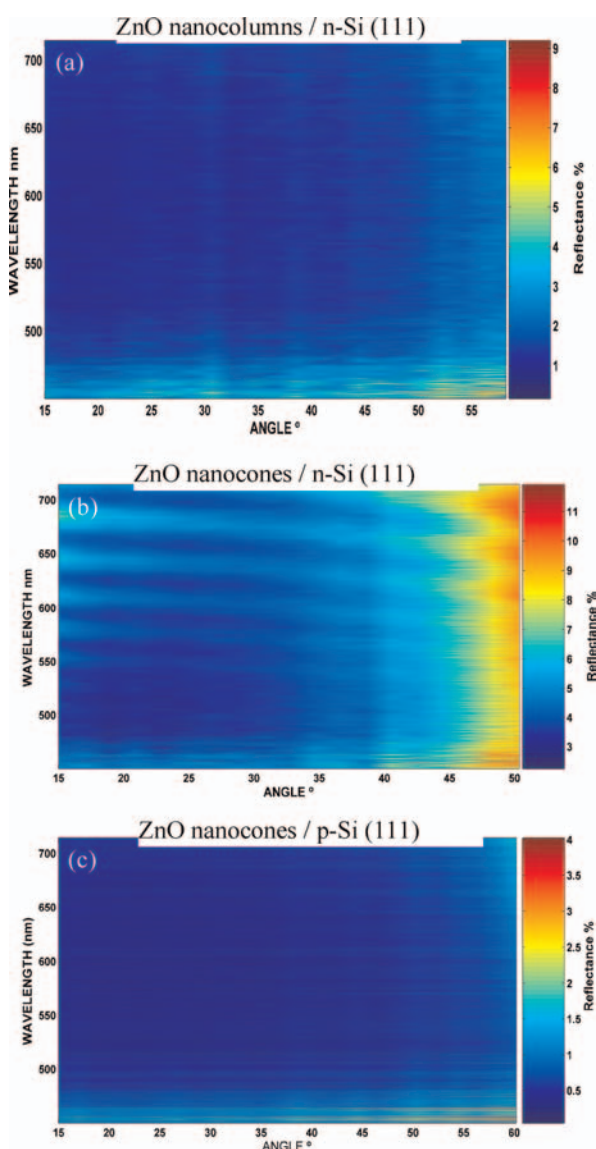
From Fig. 4 (a, b and c) the reflection from the nanostructured surfaces at 650 nm was  $\sim 1.5$  and 0.5%, over almost the whole range of measured angles. These measurements indicate that the ZnO nanostructures act as broadband antireflection coatings. The use of silicon substrates precluded transmission measurements at visible wavelengths, so the effect of the light scattering by the nanostructures on the reduction of the reflection was not determined. Measurements to understand whether this reduced reflection occurs due to an enhanced absorption in the antireflection coating and/or to refractive index matching to the substrate are underway.

**4 Conclusions** The morphological and optical properties of ZnO nanostructures grown by PLD on c-sapphire and Si (111) were assessed by SEM, PL and wavelength and angle dependence reflection. SEM images showed two main kinds of morphology: high-density nanocolumn and nanocone arrays with preferential orientation perpendicular to the substrate plane. Low temperature luminescence observed upon bandgap excitation revealed optical active centres similar to those observed for bulk samples for the different analysed nanostructures, including near band edge recombination and the green band. For the ZnO nanocone-type nanostructures grown on n-Si, however, additional features with a periodic spacing of 100 meV were found. The nature and characterization of these lines is the subject of ongoing research. In order to analyse the antireflective properties of the PLD grown nanostructures RT wavelength and RT angle dependence reflection measurements were performed. The preliminary results suggest that the nanostructures act as highly effective broadband antireflection coatings.

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**Figure 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) RT reflection of the ZnO nanostructures normalized to the reflection of the silicon reference. (a) ZnO nanocolumns/n-Si (111), (b) ZnO nanocones/n-Si (111) and (c) ZnO nanocones/p-Si (111).

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