

Bright visible luminescence of self-organized ZrO₂ nanotubes

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Abstract Self-organized nanotubular layers of ZrO₂ are electrochemically grown by tailored anodization in an (NH₄)₂SO₄ electrolyte containing small amounts of fluoride ions. The structure and morphology of these nanotubular layers were characterized by electron microscopy. XRD-measurements revealed anodic ZrO₂ films to be crystalline. Luminescence properties were investigated by photoluminescence and cathodoluminescence measurements. In both methods a very bright white luminescence of as-grown ZrO₂ nanotubes is observed. While the origin of this luminescence is not entirely clear, the findings may provide a path towards optoelectronic applications of ZrO₂ nanotubes.

Keywords ZrO₂ nanotubes · Luminescence

Introduction

ZrO₂ is an interesting material for many devices and applications in the field of ceramics, catalysis, and photonics [1–3]. This is due to its unique properties such as a high mechanical, chemical, and temperature stability. On the other hand, also the semiconductive nature is exploited due to the specific optical and electronic features of the material. The main focus of research towards optical applications is on the use as a host matrix [4–6] for incorporation of luminescence centers [7, 8]. Usually these applications require nanocrystals with a high surface area—this typically is achieved by sol-gel methods [9, 10].

Recently Tsuchiya et al. showed in a novel approach, that is the tailored anodization in fluoride ions containing (NH₄)₂SO₄ electrolytes [11, 12], how to grow highly ordered ZrO₂ nanotube systems. Even more recently, this approach could be improved using organic-based electrolytes to increase the nanotubular ordering [13] or alternatively to create highly ordered porous systems [14]. While the detailed mechanism of ordered ZrO₂ porous or tubular structures is still unclear it resembles the sister material TiO₂ (see Ref. [15] for an overview). ZrO₂ tubes grown in aqueous (NH₄)₂SO₄/NH₄F have a distinct morphology with diameters of approximately 60 nm and can reach, depending on the anodization time, up to 20 μm. Such tubes are particularly interesting as it is well known that as-grown anodic ZrO₂ is crystalline [16, 17]—this is in contrast to most other anodic valve metal oxides. In this work we show that these nanotubular arrays can be excited to yield a bright visible luminescence at room temperature which may be of high interest in optoelectronic applications of ZrO₂.

Experimental

Zr samples for anodization were cut from a commercial foil (0.1 mm thick, purity 99.8 %, Goodfellow, England) and chemically polished by dip-etching in HF–HNO₃–H₂O (1:4:2). To obtain ZrO₂ nanotubes, the zirconium samples were anodized at 20 V_{Ag/AgCl} in 1 M (NH₄)₂SO₄+0.5 wt.% NH₄F for 40 min after a potential sweep from 0 V to 20 V_{Ag/AgCl} with a sweep rate of 1 V s⁻¹. After the treatment, the samples were immediately rinsed with DI water and then dried with a N₂ stream. The nanotubular layers have visually a grayish appearance. For reference purposes 50-nm thick compact ZrO₂ layers, showing a typical blue interference color, were grown on Zr in a

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fluoride-free 1 M $(\text{NH}_4)_2\text{SO}_4$ electrolyte at 20 $V_{\text{Ag}/\text{AgCl}}$. These electrochemical treatments were carried out using a high-voltage potentiostat Jaissle IMP 88 PC (IPS Schrems, Germany).

For morphological characterization of the layers, a Hitachi SEM FE 4800 field emission scanning electron microscope (FE-SEM) and a transmission electron microscope Phillips CM 30 T/STEM were employed. The crystalline structure of the samples was determined by XRD measurement (X'pert Philips MPD PW 3040) using $\text{Cu K}\alpha$ radiation. Photoluminescence (PL) experiments were carried out using a He–Cd laser (Kimmon) for excitation at 325 nm with a power of 20 mW. The emitted luminescence spectra of the samples were recorded by a

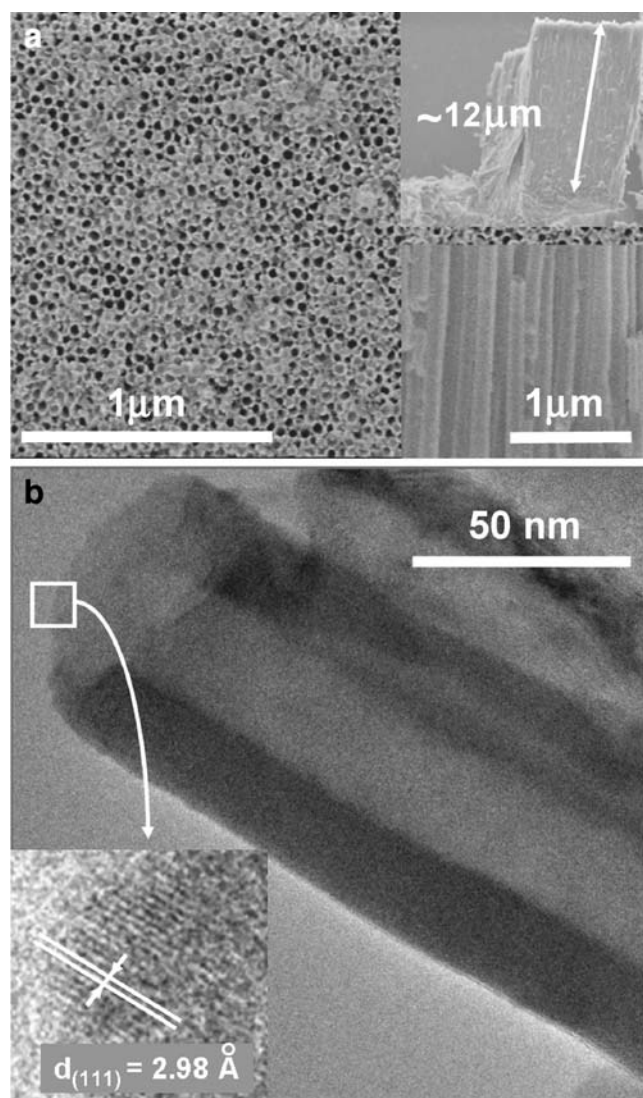


Fig. 1 **a** SEM top view and cross-sections (*insets*) of ZrO_2 nanotubes formed anodically in 1 M $(\text{NH}_4)_2\text{SO}_4 + 0.5$ wt.% NH_4F electrolyte at 20 V for 40 min and **b** TEM-image of a single ZrO_2 nanotube. The *inset* shows HRTEM image of cubic crystal planes (111) with a $d_{(111)}$ -spacing of 0.298 nm

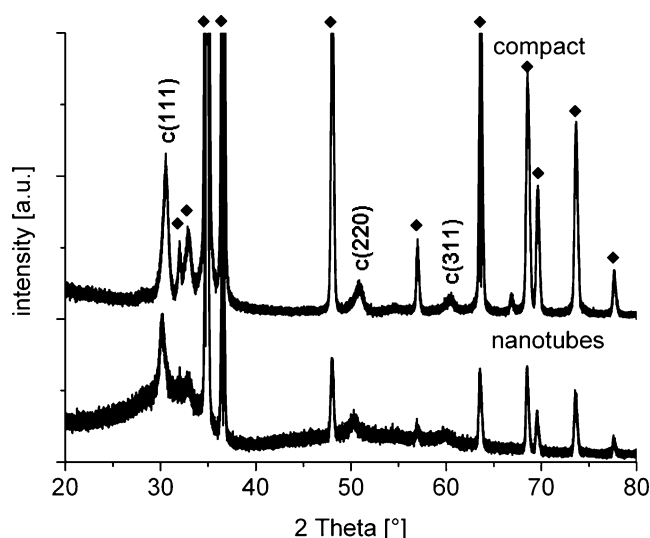


Fig. 2 XRD spectra of a nanotubular ZrO_2 layer and of a 20 V compact anodic film (peaks attribute to the metallic Zr substrate are marked with filled diamond)

setup consisting of a monochromator (Oriel cornerstone 260 1/4 M) and a photomultiplier detection system (Oriel, 7070). The monochromator was equipped with a 1,200 lines/mm grating and the slits were set to 1 mm. Cathodoluminescence (CL) measurements were performed in a SEM (Jeol JSM 6400) equipped with a parabolic, Al-coated mirror for light extracting (Oxford instruments, CL302), by fast scanning with the electron beam over a 0.1×0.1 mm square. The energy of the e-beam was alternated between 5 and 20 keV while the beam current was fixed to 80 nA. The luminescence spectra were recorded by a peltier-element cooled CCD camera system (Jobin Yvon, CCD 3,500 V) mounted on a monochromator (Jobin Yvon, Triax 320). The monochromator provided a 150 lines/mm grating and the entrance-slit was set to 1 mm. The accumulation time of the CCD for collecting the spectra was 60 s. All luminescence experiments were carried out at RT and all spectra were corrected for spectral responses of the detection systems.

Results and discussion

Figure 1a shows a top view SEM image of the nanotubular ZrO_2 layer produced in the anodization process. The two inset pictures show cross-sections of the layers—they show the ideal alignment of the single tubes in an array. A layer thickness of approximately 12 μm can be determined. Figure 1b shows a TEM image of a single ZrO_2 nanotube that confirms the tube diameter observed by SEM of ~ 60 nm and shows the tube wall to have a thickness of approximately 17 nm. The inset shows a HRTEM picture clearly demonstrating the presence of crystalline phases. An evaluation of

the lattice plane distance results in a d -spacing of ~ 0.298 nm matching to $d_{\text{cubic}}(111)$. This is in line with observations made by Tahir et al. [18] on cubic ZrO_2 nanoparticles and confirms the XRD results shown below in Fig. 2.

Figure 2 presents X-ray diffraction spectra of the nanotubular layer and a 20 V compact anodic oxide film. It is reported that anodic films on Zr in most electrolytes under high voltages are crystalline and favor a cubic/tetragonal structure or a mixture of cubic and monoclinic phases [16, 17]. This effect is also present in the XRD-measurements where a cubic crystal structure is found in the compact film as well as in the nanotubes. This is a particular feature of ZrO_2 in contrast to other valve metals, where after anodization a post-temperature treatment is necessary to convert the as-grown amorphous phase to a crystalline structure.

Figure 3 shows the photoluminescence spectra of the anodic layers. It is evident that a very strong luminescence signal is obtained from the nanotubular surface, while the reference ZrO_2 layer shows a PL that is orders of magnitude lower. The inset is an optical image taken with a CCD-camera that demonstrates the brightness of the white luminescence of the ZrO_2 nanotube layers in the dark (easily visible by naked eye). The illuminated area is 2 mm in diameter. In contrast, for the anodic compact films only a poor purple gleam is visible (in accordance with spectrum in Fig. 3). Despite the fact that a number of publications are available on the luminescence of stabilized zirconia and thermally grown oxide films [19–25], no work seems to have investigated the luminescence of anodic films or nanotubes. The origin and detailed mechanism of the luminescence from ZrO_2 , in particular the role of over mid-gap states is still unclear and controversially discussed

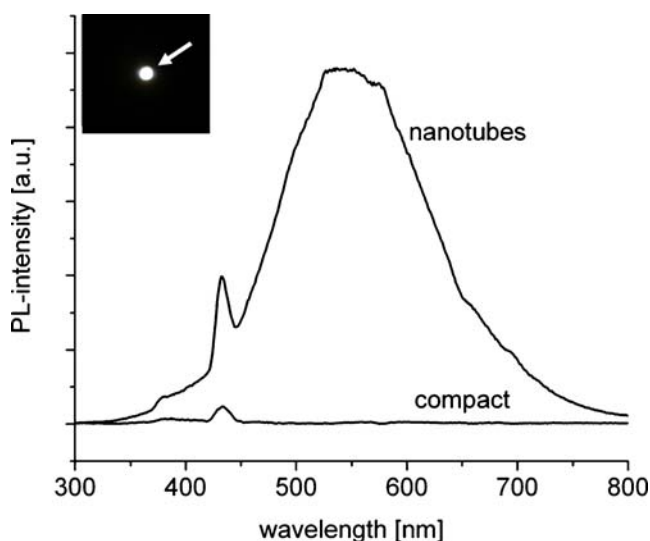


Fig. 3 Photoluminescence spectra of the ZrO_2 nanotubes and the compact anodic film by illumination with 325 nm, *inset* is a CCD picture of the luminescence

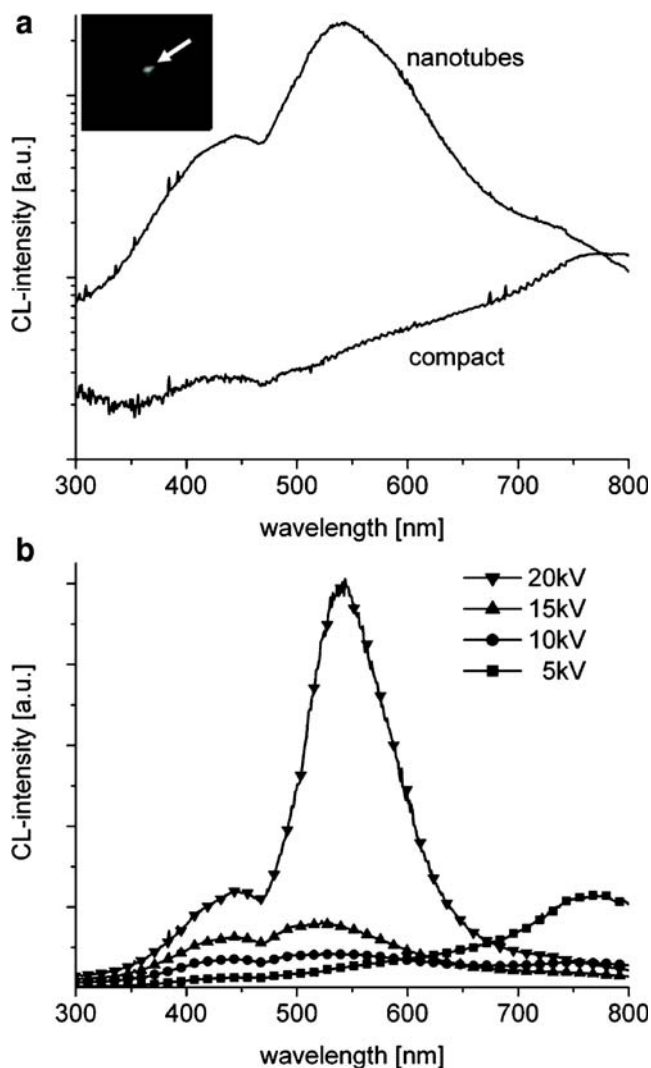


Fig. 4 **a** Cathodoluminescence spectra of the ZrO_2 nanotubes and the compact anodic film, *inset* is a CCD picture of the luminescence. **b** CL-spectra of the nanotubular layers for various acceleration voltages of the e-beam from 5 to 20 keV

in literature. Latest work attributes the luminescence either to be truly intrinsic, i.e. from strong localized regular complexes, or to stem from oxygen vacancies in a complex with other alloying elements or impurities (Fe, Cr, Hf) in the nearest cation shell. It is reported that also the surface reconstruction (unsaturated Zr sites) and the crystalline phases (monoclinic, cubic or tetragonal) influence the luminescence [26, 27]. In the spectra of Fig. 3 one can clearly see that the response (in particular of the tubes) consists of several peaks with shoulders over the whole range of visible light which confirms the observed white visible light impression to the eye. The luminescence of the compact film is significantly lower.

Figure 4a shows the results of the CL-measurement in a logarithmic scale. The results are in line with PL characterization. Clearly the nanotubes have a significantly higher

total luminescence than compact films. The inset is a CCD picture of the white luminescence of the ZrO₂ nanotubular array taken in the SEM. The illuminated area was 0.01 mm². A comparison with the PL-spectra only shows significant differences in the peak intensity but only small differences in the peak spectral distribution. These differences can be ascribed to the energies of the excitation beams, used gratings 1,200 lines/mm vs. 150 lines/mm in the two monochromators and the different exposure times. The differences in peak intensity must be ascribed to other factors. A key difference between the measurements is that a 20 keV electron beam can easily excite electrons into the conduction band of ZrO₂ (bandgap of ~5 eV) while for UV light with 325 nm this is impossible. Also due to the much higher excitation densities in CL, the created electron-hole pairs may favor a different recombination path. Thus it is not surprising that peaks arising at higher wavelength (700–800 nm) are mainly observed by CL-measurements [28] and are not present in the collected PL-spectra. DFT calculations of point defects in monoclinic zirconia [29] suggest that additional charges (here given by the e-beam) can influence the electric levels of these defects and therefore change their optical behavior.

Figure 4b shows the change in the CL of nanotubes by alternating the acceleration voltage. Interestingly for 5 keV the shape of the spectra is somehow similar to compact films, whereas increasing the beam energy a broad peak at around 550 nm arises. The spectrum obtained at 20 keV matches the PL-spectrum. In principle, increasing the acceleration voltage of the e-beam increases the interaction volume in the sample (increasing penetration depth). Hence, high beam energies can deliver a bulk (whole tube layer) response whereas small energies lead to more surface (tube-tops) related information. In other words, for higher excitation more luminescence attributed to the self-organized nanotube morphology and surface contributes to the spectra, which results in the final bright white luminescence.

Overall the observed PL and CL spectra for the nanotubes are in line with literature data [26–28] that interpret the luminescence to stem from mid-gap states (intrinsic or surface) rather than from any quantum size features within the tube walls and thus may be attributed to the unique morphological and surface properties of self-organized anodic ZrO₂ nanotubes.

Conclusions

In this work we presented for the first time results on the bright luminescence observed for as-grown anodic ZrO₂ nanotubular arrays. The visually observed shiny white light impression after excitation was obtained and confirmed by independent experiments (photoluminescence and cathodo-

luminescence). The origin of the luminescence is not entirely clear but consistent with the classical mid-bandgap states in ZrO₂ that may be either of intrinsic or surface-related nature.

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