

Intense white photoluminescence in ZnO thin film formed by anodization

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Intense white photoluminescence (PL) at room temperature has been observed in ZnO thin films formed by anodization at 26°C. The PL depends on the preparation conditions of the films. The PL is attributed to radiative recombination between localized electrons and holes in gap states which are formed by native defects in the films. We suggest that the anodized ZnO films might be useful for optoelectronic devices, since the low temperature anodization process used is inexpensive and fast.

1. Introduction

Recently, there has been a great deal of interest in large-area ZnO thin films for use in display [1, 2] or photovoltaic [3-6] devices. This material lends itself to a variety of thin film deposition techniques: sputtering, vacuum evaporation, vapour transport, spray-pyrolysis and anodization. There are few reports [1, 2] on the application of thin film deposition techniques to such display devices, although ZnO films formed by painting phosphors have been used in cathode ray tube and vacuum fluorescent devices [7]. In ZnO thin films formed by sputtering, relatively efficient blue-green and red electro- and photoluminescences have been realized in recent years [1, 2, 8]. However, these films required deposition on high temperature substrates or post-deposition preparative treatment to achieve such efficient luminescence. In this paper, we report the observation of intense white PL in thin films of ZnO formed electrochemically at low temperature of 26°C by anodization and the dependence of the luminescent properties on anodization conditions. The anodization process which is inexpensive and fast does not essentially require a high temperature technique and might also be useful for application to optoelectronic devices.

2. Experimental procedure

Anodized films were formed on zinc plates cut from 99.999% high purity zinc sheet or on zinc

films deposited on conducting solids by using vacuum evaporation and plating techniques. A platinum cathode was used and both electrodes were connected to a regulated d.c. power supply. The anodizing electrolyte was potassium hydroxide [9-13] in aqueous solution with different concentrations in the range of 0.1 to 2.0M. The electrolyte was held at a constant temperature of 26°C during the anodization. All anodized films were formed by a two step process: first a constant current anodization and then a constant voltage one. If a constant voltage anodization is carried out without a constant current anodization, in the initial stage of growth very high current densities are required and consequently a constant growth rate cannot be kept throughout the anodization process. One way round this difficulty is to anodize under constant current conditions until the desired anodizing voltage (V_d) is reached. In the first anodizing step, samples were anodized at a constant current density of 150 mA cm^{-2} until V_d was reached. In the second step, after V_d was reached, samples were held at V_d for 60 min. The film thickness was measured by using a surface roughness detector. The films were evaluated using a conventional X-ray diffractometer with a copper target and with a scanning electron microscope. The PL measurement was carried out using excitation by a pulsed nitrogen laser (N_2 -laser) or continuous wave (cw) ultra-high pressure mercury lamp (Hg-lamp). The PL was

dispersed by a monochromator, detected by a cooled photomultiplier followed by a box-car integrator which could be appropriately gated. All PL spectra were corrected for the diffraction efficiency of the grating and the optical response of the photomultiplier.

3. Results and discussion

The anodized ZnO films were formed in limited ranges of both the electrolyte concentration (0.1 to 2.0 M) and the anodizing voltage ($V_d = 1$ to 60 V), and their colours were black and white as shown in Fig.1. Films anodized at $V_d < 7$ V were black. Such films were relatively thin and had a smooth surface. However, films anodized at $V_d > 9$ V and electrolyte concentration between 0.1 and 0.5 M were white. These films having a minimum thickness around $10 \mu\text{m}$, were porous. For the region without hatching in Fig. 1, the formation of anodized films was difficult because the formed films flake off in some spots. Fig. 2 shows typical PL spectra for the black and white films. The PL was measured using N_2 -laser excitation at room temperature (RT). These spectra consist of a sharp ultraviolet emission band (≈ 380 nm) and a very broad visible emission band (≈ 580 nm). In this paper, we did not mainly concern ourselves with the luminescent properties of the ultraviolet emission band, which is attributed to excitonic recombinations [14–16]. The PL for the two films differed in intensity and linewidth.

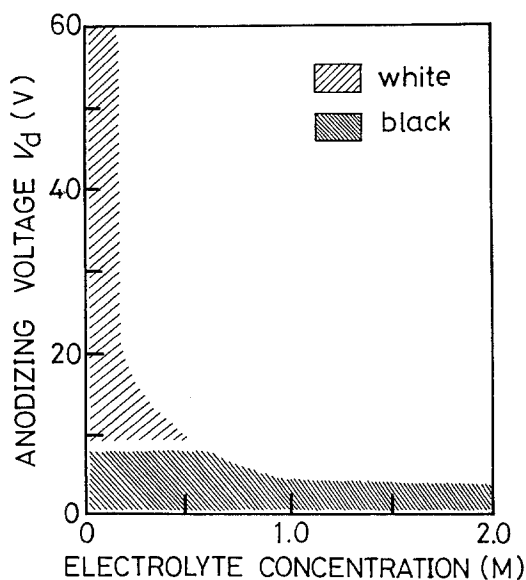


Figure 1 Dependence of the film colour on the electrolyte concentration and the anodizing voltage (V_d).

The typical half-width for white and black films were 0.91 and 0.74 eV, respectively. The white films had an integrated PL intensity of the order of 4 greater than the black films. In white films, the PL was white and very intense, and the dependence of the intensity on V_d ($V_d > 9$ V) was not observed. The intensity was approximately comparable to that of P24 phosphors (ZnO:Zn) under N_2 -laser excitation.

The temperature dependence of the PL intensity of white films from liquid nitrogen temperature (LNT) or RT is shown in Fig. 3. Over this temperature range, the half-width and the peak position of the spectrum remain unchanged, but the intensity decreases exponentially with a low-temperature exponent of about 9 meV and a high-temperature exponent of about 37 meV. In this temperature range, the PL showed non-exponential decay, consisting of a fast decay having a time constant below about $0.2 \mu\text{sec}$ and a slow one of $3 \mu\text{sec}$ at LNT. The time constants at RT were decreased by roughly a factor of 2 from LNT. Fig. 4 shows time-resolved PL spectra at LNT. The dashed line in the figure shows the PL spectrum on cw Hg-lamp excitation [17]. The intensity at higher energies in the spectra was more rapidly decreased during decay. This implies that there exist other emission bands with longer decay times at low energies [2].

Up to the present, four emission bands have been reported in PL measurements of single crystal and polycrystalline ZnO [14–16, 18–26]; (a) ultraviolet emission, (b) blue–green emission, (c) yellow–red emission and (d) infrared emission. The centres responsible for all except the ultraviolet emission, although extensively studied, are still the subject of much controversy. Recently, we have reported that in sputtered polycrystalline ZnO films PL in the wavelength range from blue–green to red could be observed and depended on the preparation conditions [2]. The features which have been observed on PL measurements of such samples are as follows: (a) the broad emission spectrum was observed at very low energy rather than the band-gap energy, (b) the intensity and the linewidth of the PL depended on the sample preparation conditions, (c) the PL decay was non-exponential and (d) on time-resolved PL measurements, the intensity at high energies in the spectrum was more rapidly decreased. These features were also observed in our anodized films. It should be noted that the PL spectrum in

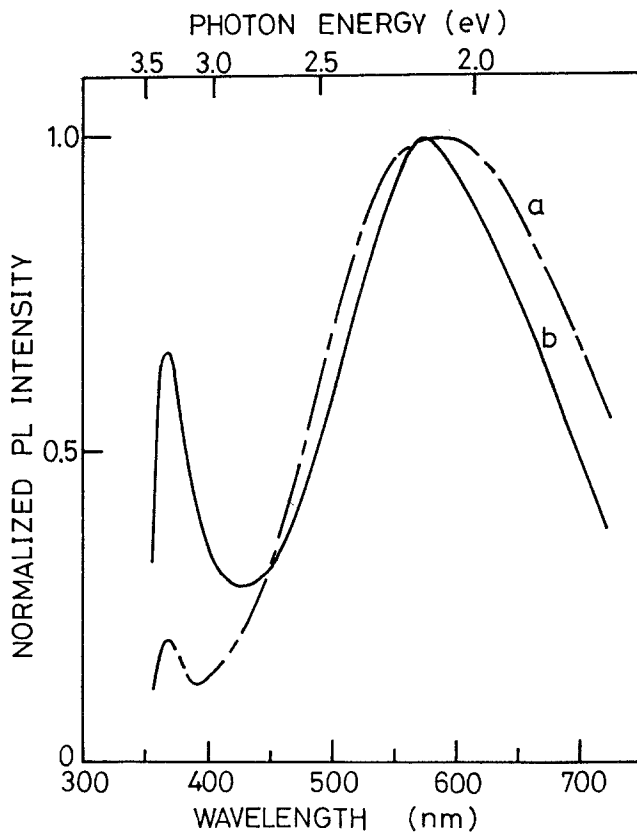


Figure 2 Normalized PL spectra for the white (curve a) and the black (curve b) anodized ZnO films.

anodized films was very broad compared with that in sputtered films. While the PL spectrum in sputtered films could be separated into three emission bands (blue-green, red and infrared emissions) which depended on the preparation conditions. Fig. 5 shows excitation spectra for

white PL in anodized films and blue-green and red PLs in sputtered films. It is clear from the figure that these PLs resulted from band-to-band excitation of ZnO with a band gap of 3.4 eV. In our previous papers [2, 8], we attributed the visible PL in sputtered films to native defects.

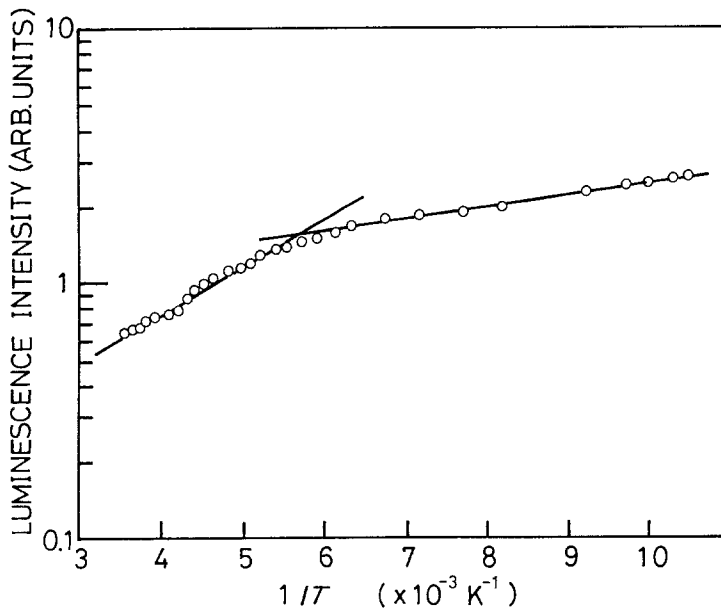


Figure 3 PL intensity of the white film as a function of temperature (T).

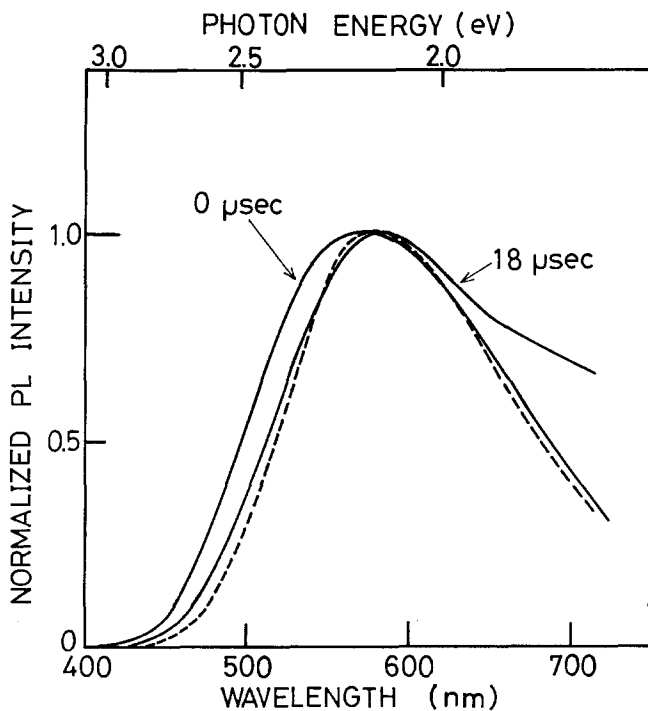


Figure 4 Time-resolved PL spectra of the white films under pulsed N_2 -laser (solid line) and cw Hg-lamp (dashed line) excitations at LNT. The time delay from the pulse excitation is shown in the figure.

The native defects in ZnO might form energy levels in the band gap [19] and they might act as electron- and hole-trap centres in radiative recombination processes. One might expect that anodized films also contain a large number of native defects [10, 13] responsible for the blue-green and the red emissions. By X-ray diffraction analysis and scanning electron microscopy, we found that the anodized films were polycrystalline ZnO with much smaller crystallites and grains than sputtered films. The typical crystallite sizes (ΔL) of anodized and sputtered films were $\Delta L \approx 10$ nm (a black film was larger than a white film) and $\Delta L = 30$ to 40 nm, respectively. This fact suggests that the PL linewidth in anodized films may be dominated by disorder broadening. This is supported by the following: (a) the linewidth of white PL was independent of the temperature, (b) the linewidth increases with decreasing the crystallite size which depends on the preparation conditions and (c) the half-width of the ultraviolet emission (≈ 380 nm) due to exciton recombination in our anodized films was above 35 nm, larger than that in polycrystalline samples (> 20 nm) [16] and single crystals (≤ 15 nm) [27]. In recent years, intense PL with linewidth dominated by disorder has also been observed in plasma-deposited amorphous Si:H [28, 29], Si:O:H [30], spray-pyrolysed polycrystalline CdS [31, 32] and CdTe

[33] films. In PL measurements on these films without intentional impurity doping, the broad emission spectrum has been observed at energies well below the band-gap energy. It has been understood that these broad PLs are caused by radiative transitions between localized gap states. Therefore, we suggest that this is also the situation in anodized ZnO films. In our case for anodized films, the gap states may be formed by the native defects responsible for blue-green and red emissions being extended because of disorder broadening. However, we cannot neglect the possibility of doping of impurities such as alkali metals [21] and copper [20] during the anodization process. These impurity centres act as deep hole traps responsible for visible PL in ZnO.

Our most striking result is the very intense white PL at RT. Under identical PL measurements, anodized films have a PL intensity of the order of 3 greater than that of as-deposited sputtered films. Some of the defects and imperfections which are created in sputtered or anodized films might act as non-radiative recombination centres. In sputtered ZnO films, we reported that the PL efficiency is dominated by the non-radiative recombination process [2, 34]. Sputtered films are exposed to bombardment by high-energy particles during the deposition process and consequently many damage defects which act as non-

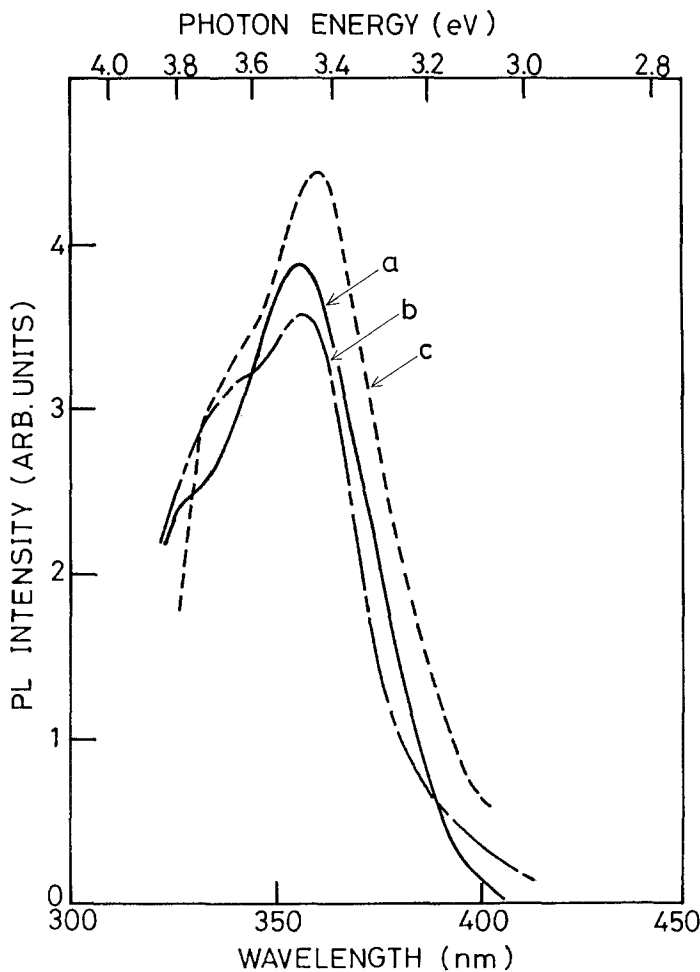


Figure 5 Excitation spectra for white PL (curve a) in anodized film and blue-green (curve b) and red (curve c) PLs in sputtered films at LNT.

radiative recombination centres may be formed. However, anodized films might contain a smaller number of such damage defects, giving rise to more intense PL. In PL caused by radiative transitions between localized gap states, generally, an electron and a hole at deep traps have a very localized wave function regardless of the origin of the traps [19–21], so hence tunnelling to non-radiative centres may also be reduced [31]. On the other hand, we suggest that the native defects which act as radiative recombination centres are formed in white films more so than in black films and sputtered films because of the different crystallinity of films caused by the preparation conditions [2, 8]. These explain the fact that the white PL due to radiative recombination between localized gap states in anodized ZnO films with many defects and imperfections is intense.

In electroluminescent cells incorporated using these anodized films and mica insulators, we

could observe yellowish white electroluminescence under a.c. drive. The brightness of the luminescence was about 1 ft-lambert. Also we could observe white luminescence from anodized films which were excited by low-voltage electrons. These facts suggest that the anodized ZnO films might be useful for display device applications.

4. Conclusions

We observed intense white PL in anodized ZnO films formed at low temperature (26°C) in a potassium hydroxide solution. The intensity and the linewidth of PL depended on the preparation conditions, and the linewidth was dominated by disorder broadening. The white PL was attributed to the transition between a trapped electron and hole in localized gap states which were formed by native defects. We also observed relatively intense white electro- and cathodoluminescences in anodized films. Since the anodization process used is inexpensive and fast, anodized ZnO films

might be useful as a less expensive material for display devices.

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