A Novel Method for the Preparation of Green-photoluminescent Zinc Oxide by Microwave-assisted Carbothermal Reduction

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We succeeded in preparing green-photoluminescent zinc oxide (ZnO) by microwave-assisted carbothermal reduction in air. This method enables us to control the maximum green-PL intensity by changing the percentage of carbon reacted under microwave irradiation for only 2 min at 650 W.

Zinc oxide (ZnO) has attracted much attentions to dye-sensitized solar cell (DSC) electrodes,[1] antireflection (AR) coatings,[2] photocatalysts,[3] varistors,[4] photonic crystals,[5] surface acoustic wave (SAW) filters,[6] ultraviolet (UV) semiconductor diode lasers (SDLs),[7] UV photodetectors,[8] photodiodes,[9] optoelectronic devices,[10] and gas sensors[11] owing to excellent chemical- and thermal-stabilities, a wide bandgap (3.37 eV), and a large exciton-binding energy (60 meV). In particular, green photoluminescence (PL) of ZnO phosphors has recently attracted much interest because of its potential use in a low-voltage cathodeluminescence (CL) phosphor for low-voltage field emissive displays (FEDs) in flat panel displays area.[12] Green PL of bulk or powder ZnO has been observed by sintering in air at 1073–1673 K for 2–10 h or in forming gas (N_2:H_2 = 95:5) at 773–1173 K for 20 min.[13,14]

Microwave (MW) heating offers several advantages for the synthesis of inorganic materials compared to conventional methods.[15] The greatest advantages appear to be the very short timescales involved in the preparation and the selective heating due to the selective interaction of MW with substances. Carbon (C) is known to act as a reduction agent and heated rapidly under MW irradiation because it efficiently couples with electromagnetic radiation, creating heat owing to the Joule effect.[15] MW-assisted carbothermal reductions have been performed for preparing metal oxides (MoO_2, Cr_2O_3, VO_2, VPO_4, Ag+MoO_2),[16] metal nitrides (TiN, GaN, VN),[17] Al_2O_3 + mullite + SiC,[18] and β'-SiAlON.[19] But to our best knowledge, PL-characteristic control of metal oxies by MW-assisted carbothermal reduction has not been reported. Herein, we first report the novel preparation of green-PL ZnO by MW-assisted carbothermal reduction in air under MW irradiation only for 2 min at 650 W.

The synthesis of green-PL ZnO was carried out using powder zincite ZnO 0.1–0.5 g (Mitsui Kinzoku Kogyo Co., >99.5%, particle-size range from 0.1 to 3.9 μm, d_{50} = 0.8 μm) and activated carbon 0.05 g (Wako, particle-size distributions of 2–10% (100 mesh on), 10–20% (100–200 mesh), 10–20% (200–300 mesh), and 55–75% (300 mesh pass)) as starting materials at the percentage of carbon reacted 0–33 wt %. A domestic MW oven (Sanyo EM-650T, a maximum power output of 650 W and a magnetron frequency of 2.45 GHz) modified by Shikoku Keisoku Kogyo Co. (ZMW-002) was employed for MW irradiation. The ZnO powder and activated carbon were well mixed and placed on a glass wool sheet. Each mixture turned to red-hot under MW irradiation of 2 min at 650 W output power. The reaction temperatures could not be measured by a thermocouple because of a spark induced by MW irradiation.[20] After MW irradiation the products were cooled inside the oven. The product powder became to be quite white color, and carbon was found to be almost completely burnt out. The structures of the products were examined using powder X-ray (Cu Kα) diffraction (XRD) patterns (Rigaku Multiflex). From the XRD patterns we detected only zincite ZnO (powder diffraction file, PDF #36-1451) after MW irradiation. UV–vis absorption spectra (Jasco V-570) of ZnO both before and after MW irradiation were recorded. The absorption spectrum was found to shift to longer wavelength after MW irradiation. This change of the band structure of ZnO was probably caused by a Burstein–Moss shift due to a change in free carrier concentration.[21] The oxygen vacancies were created by MW-assisted carbothermal reduction, resulting in increase of the concentration of free carriers in ZnO.

The fluorescence was generated at room temperature by continuous-wave, near-UV excitation at 380 nm from a Xe lamp filtered by a single monochromator (Hitachi U-4500) as shown Figure 1. The peaks of the green PL spectra shifted from 525 to 510 nm after MW irradiation. The 525-nm emission peak would be attributed to Frenkel-pair complexes involving an oxygen vacancy, while the 510-nm peak could be attributed to the isolated singly occupied oxygen vacancies ($V_o^{\bullet}$) centers.[22] The green 510-nm PL of ZnO observed by excitation at 380-nm excitation was found to be strongly dependent on the percentage of carbon reacted in the starting mixtures. Figure 2 shows that the intensity of the green 510-nm PL was increased with increase at the percentage of carbon reacted from 0 to 17 wt %, but was decreased with increase at its percentage from 17 to 33 wt %. As a result, the maximum green 510-nm PL intensity was found at the percentage of carbon reacted of 17 wt %.

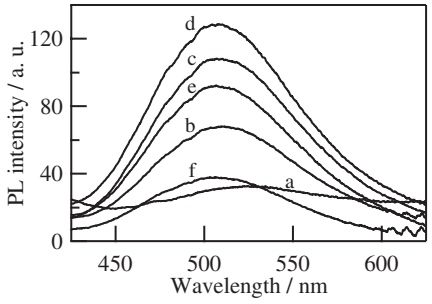

Figure 1. PL spectra of ZnO excited at 380 nm (a) before MW irradiation and after MW-assisted carbothermal reduction for 2 min at 650 W at the percentage of carbon reacted (b) 9 wt %, (c) 14 wt %, (d) 17 wt %, (e) 25 wt %, (f) 33 wt %.

The singly occupied oxygen vacancies ($V_o^{\bullet}$) has been observed at $g \approx 1.96$ by electron spin resonance (ESR).[14] The signal with $g \approx 1.96$ was observed after MW-assisted carbothermal reduction, though no signal was observed before the reduction. The relative $V_o^{\bullet}$ density was calculated by a double integration of the area of the resonance lines at $g \approx 1.96$. A good correlation was found between the green-PL intensity and the relative $V_o^{\bullet}$ density up to 20 wt % (Figure 2) as reported for the reaction of ZnO with H_2.[14] In the range more than 25 wt %, the relative $V_o^{\bullet}$ density did not decrease despite decreased green-PL intensity.

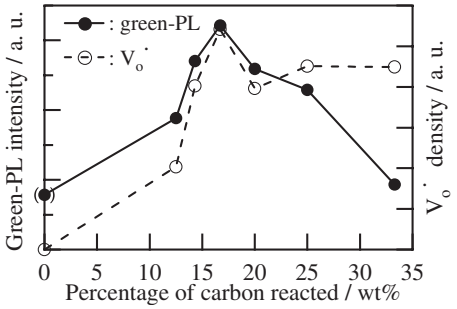

Figure 2. Green PL intensity (510 nm) of ZnO excited at 380 nm and the relative $V_o^{\bullet}$ density as a function of the percentage of carbon reacted after MW-assisted carbothermal reduction for 2 min at 650 W.

Figure 3 shows the excitation spectra for ZnO observed at 510 nm at room temperature. The excitation spectra for the PL emission had the peaks around 380 nm and showed the PL emission at the longer wavelength than the absorption edge in UV–vis spectra, suggesting the presence of the $V_o^{\bullet}$ level in the band gap of ZnO.

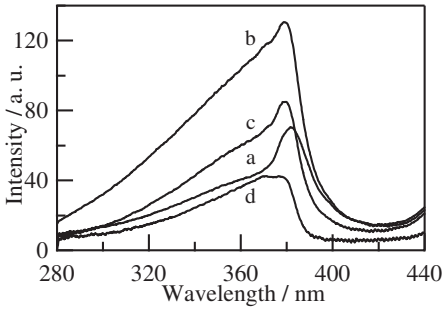

Figure 3. Excitatation spectra of ZnO monitored at 510 nm at the percentage of carbon reacted (a) 9 wt %, (b) 17 wt %, (c) 25 wt %, (d) 33 wt % after MW-assisted carbothermal reduction for 2 min at 650 W.

When ZnO is reduced in forming gas N_2:H_2 = 95:5 from at 773–1173 K, the following reaction may occur as $ZnO + xH_2 \rightarrow ZnO_{1-x} + xH_2O(g)$, $ZnO_{1-x} \rightarrow Zn_{1-y}O_{1-x} + yZn(g)$. Whereas in MW-assisted carbothermal reduction, which would be more imhomogeneous compared with gas-solid reaction between H_2 and ZnO, the formation of oxygen-deficient structures can be written as $ZnO + xC \rightarrow ZnO_{1-x} + xCO(g)$, $ZnO_{1-x} \rightarrow Zn_{1-y}O_{1-x} + yZn(g)$. Vanheusden et al. reported that the green PL in ZnO phosphores is due to the recombination of electrons in singly occupied oxygen vacancies ($V_o^{\bullet}$) with photoexcited holes in the valence band.[14] With increase of the percentage of carbon reacted from 0 to 17 wt %, MW-assisted carbothermal reduction accelerates the generation of oxygen vacancies $V_o^{\bullet}$ in ZnO_{1-x}, which might act as the recombination centers for the electron–hole pairs. But, with increase of the percentage of carbon reacted from 17 to 20 wt %, the sample temperature will be too high under MW irradiation. Therefore, the amount of released Zn(g) as vapor may be increased at high temperature, and ZnO_{1-x} may change to $Zn_{1-y}O_{1-x}$. As a result, decrease of $V_o^{\bullet}$ in $Zn_{1-y}O_{1-x}$ will reduce green PL intensity. The discrepancies between the green-PL intensity and the relative $V_o^{\bullet}$ density observed at the percentage of carbon reacted more than 25 wt %, especially 33 wt %, need to be investigated further.

In summary, we succeeded in preparing of green-PL ZnO by MW-assisted carbothermal reduction in air. This method enables us to control the maximum green PL intensity at the percentage of carbon reacted 17 wt % for only 2 min at 650 W.

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