Synthesis and Luminescent Properties of Strong Blue Light-Emitting Al2O3/ZnO Nanocables

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Photoluminescence measurement indicates that a strong blue emission peak at ~450 nm appears at 400 and 600°C in O2 and N2 atmospheres, respectively. A 30% enhancement of the relative intensity ratio of blue emission (Ib) to ultraviolet emission (IUV) has been observed for the Al2O3/ZnO nanocables. High-resolution transmission electron microscopy and X-ray photoelectron spectroscopy analyses reveal that the origin of the strong blue emission can be attributed to the structure transition and cleavage of the oxygen–hydrogen bond (OH) of the Al2O3/ZnO nanocable, which leads to the formation of singly ionized oxygen vacancies (Al–O2−). © 2008 The Electrochemical Society. DOI: 10.1149/1.2890289 All rights reserved.

Al2O3 has been used for capacitor dielectrics and gate oxides in memory devices due to its high dielectric constant, very low permeability, and high thermal conductivity. However, the photoluminescence (PL) property of alumina film or nanoparticles has not been studied in detail. Yoldas et al. studied alumina–silica powders and stated that the presence of pentahedrally coordinated aluminum appears to be strongly correlated with the occurrence of PL. Suga et al. studied alumina gel from an inorganic salt and alkoxide, and mentioned that the PL is closely related to oxygen defects and the development of the Al3+ site. However, no data exist for determining the dependence of the properties of a defect center on the structure of its coordinate sites and the presence of luminescence. Recently, Li et al. reported that a broad band located around 422 nm could be detected from nanosized γ-Al2O3 powder. It is suggested that the produced defect level could induce γ-Al2O3 nanopowder to emit blue PL bands. However, most of those studies have focused on nanopowders or gel films. In past years, ZnO/Al2O3 core/shell nanofibers have been prepared from the Al2O3 deposition of ZnO nanowires with an atomic layer deposition technique, but no PL properties have been reported. These findings indicate that so far, the PL property of nanoscale alumina film has not been investigated. In addition, our previous study found that, when an alumina film is deposited on a ZnO-coated silicon substrate, the thickness of the alumina shell on the ZnO nanorods can be modulated by controlling the annealing temperature. After that, the ZnO nanorods were exposed to surface modification by oxygen plasma treatment, and were subsequently immersed in the precursor sol of Al3+ to grow an alumina shell on the ZnO nanorods at 80°C for 1 h. The thickness of the alumina shell on the ZnO nanorods can be modulated by controlling the reaction parameters. After washing with distilled water, rapid thermal annealing was performed for aluminum sol-coated ZnO nanorods at 200–600°C in nitrogen and oxygen atmospheres. Microstructure observation of Al2O3/ZnO nanocables was performed by using a transmission electron microscope (TEM, JEOL 2010) operated at 200 keV. Room-temperature PL measurement was performed on the nanorods, which were excited by a 325 nm He–Cd laser with an excitation power of 25 mW. The emitted luminescence light was collected through a 0.32 m spectrometer with a charge-coupled device detector. The focused spot size of the He–Cd laser was estimated to be about 200 μm in diameter. X-ray photoelectron spectroscopy (XPS) was used to evaluate the Al–O chemical binding states. The 27Al magic angle spinning nuclear magnetic resonance (MAS NMR) was used to examine the chemical shift of alumina-coated ZnO nanocables scraped from the Si substrate using a Bruker Dxs400w NMR spectrometer. The XPS analyses were performed on a Kratos AXIS Ultra with a monochromatic Mg X-ray source at 150 W.

Results and Discussion

Figure 1a shows the scanning electron microscope (SEM) surface image of the arrayed as-synthesized Al2O3/ZnO nanocables grown vertically on ZnO/Si substrates. It was found that the nanorods have a well-defined hexagonal plane with a diameter of approximately 20–30 nm. Further analysis on as-synthesized Al2O3/ZnO nanocables is shown in the TEM image of Fig. 1b,
indicating that alumina was conformably deposited on the ZnO nanorods and that the nanorods remained in their original shape. Energy-dispersive spectroscopy (EDS) analysis further confirmed that only strong Zn and O signals without Al were identified in the core nanorods, but that a weak peak corresponding to Al could be detected from the shell, indicating that an alumina shell was formed on the ZnO nanorods at low temperature.

The high-resolution (HR) TEM image in Fig. 2a illustrates that alumina was conformably deposited on the ZnO nanorods to become a core/shell Al₂O₃/ZnO nanocable structure. From the selected area electron diffraction in the inset of Fig. 2a, two diffraction patterns (rings and spot patterns) are observed. The spot pattern is from the single-crystal ZnO structure, while the ring pattern can be attributed to an amorphous alumina structure that may be a pseudo-boehmite phase developed in aqueous solution according to the report of Ishizaka. Upon annealing at 200°C, a short-range ordered structure seems to develop in the alumina shell, as shown in the HRTEM image of Fig. 2b. It is believed that rapid thermal treatment in an O₂ atmosphere is favorable for the cleavage of the oxygen–hydrogen bond, causing the departure of H ions from the pseudoboehmite and initiating the occurrence of the phase transformation of amorphous pseudoboehmite into a γ-phase alumina structure. This structure can be thought of as a cubic spinel, with some suggestion of a tetragonal tetrahedrally coordinated aluminum distortion in boehmite-derived γ-Al₂O₃ in the I₄₁/amd space group. When annealed at 400°C in an O₂ atmosphere, a long-range ordered structure can be clearly observed from the HRTEM image in Fig. 2c. According to the calculation of the lattice fringe (about 0.2 nm), it was indexed as a (400) plane, indicating a γ-phase alumina structure (d = 0.198 nm). This suggests that with increasing the temperature to 400°C in an O₂ atmosphere, the γ-phase was developed in the alumina shell. As annealed at 600°C, two kinds of lattice fringes are clearly observed for annealed Al₂O₃/ZnO nanocables as shown in Fig. 2d, indicating that, in addition to single-crystalline ZnO nanorods, a crystalline γ-alumina structure has been completely formed in the alumina shell at 600°C.

Figure 3a shows the room-temperature PL property of Al₂O₃/ZnO nanocables at different temperatures. Three important emission peaks can be observed from the PL spectrum of as-synthesized alumina-coated ZnO nanocables. Both ultraviolet (UV) emission (378 nm) and green–yellow (visible) emission (525–575 nm) bands are attributed to ZnO nanorods, and the other broad blue emission (425–475 nm) is possibly from the alumina shell. The near bandedge (UV emission) is generally attributed to free-exciton re-
combination, but the green–yellow emission is produced from the oxygen defect of the pure ZnO nanorods fabricated by chemical solution methods. In fact, it was found that the UV emission intensity of the as-grown nanocables increases with the annealing temperature at 200–600°C in an oxygen ambient, but the visible emission in postannealed samples tends to disappear, suggesting that the native defects can be reduced by postannealing treatment as shown in Fig. 3a. It was noted that when the Al2O3/ZnO nanocables are annealed at 200°C in an O2 atmosphere, an obvious blue emission at around 450 nm, which was primarily contributed from the alumina shell, can be clearly identified. According to the report of Lippens et al. and TEM analysis (Fig. 1), an increase of the annealing temperature may cause the cleavage of the oxygen–hydrogen bond (OH) in pseudoboehmite structure, and consequently, both Al–O–O’ and Al–O’ defects would probably be produced in the alumina shell and vary with annealing temperature and atmospheres. At a lower temperature, i.e., 200°C, Al–O–O’ defects are much more easily generated than Al–O’. However, according to Ishizaka’s report, the distance between the aluminum atom and the electron spin in Al–O–O’ is long enough to neglect the hyperfine interaction with Al, indicating that Al–O’–O’ would not be a luminescent center. With the increase of the annealing temperature, the OH bond in the pseudoboehmite structure tends to be broken and Al–O’ would be formed during the phase transformation from the pseudoboehmite phase (octahedrally coordinated structure) to the γ-phase aluminum oxide (tetrahedrally coordinated structure), favoring pentahedrally coordinated aluminum and the occurrence of singly ionized oxygen vacancies which are regarded as the F center.

With increasing the temperature to 400°C, dehydration proceeds and the structure evolves through a series of disordered states during the phase transformation from pseudoboehmite to γ-phase as demonstrated in Fig. 2c. In this condition, pentahedrally coordinated aluminum is easily formed, indicating that more singly ionized oxygen vacancies (F center) defects can be generated. Therefore, a strong blue emission can be observed. At a higher temperature, i.e., 600°C, although the positions of the blue emission remain unchanged, it is found that the peak intensity is weakened compared to the sample annealed at 400°C. This indicates that the defect density of the main defects (F center) responsible for the blue emission is decreased with increasing the annealing temperature up to 600°C. Consequently, the density of the F center is reduced due to compensation in the O2 atmosphere.

As reported, ZnO material usually generates a strong UV emission. However, it can be seen in the figure that UV emission decreases while blue light emission increases. It can be inferred that UV emission from the ZnO band-edge recombination can excite the blue light of aluminum oxide. This may result in different intensity ratios of blue light to UV in the PL spectra. To further investigate the effect of heat treatment on the F center and pentahedrally coordinated aluminum, the as-synthesized Al2O3/ZnO nanocable samples were subjected to annealing at different temperatures in N2 and O2 atmospheres. The relative PL ratios (Ip/IUV) of blue emission to UV emission on annealing temperature as a function of O2 and N2 atmospheres is presented in Fig. 3b. It is observed that the strongest blue emission of the nanocables appears at 600°C in a nitrogen ambient instead of 400°C in an oxygen atmosphere. Furthermore, the blue emission of postannealed Al2O3/ZnO nanocables is dominated not only by the annealing temperature but also the annealing atmosphere because the PL emission is very sensitive to defect type. As dehydration proceeds, the structure evolves through a series of disordered states, probably from octahedral to pentahedral and then tetrahedral. Ishizaka et al. reported that the luminescence is maximized for alumina treated at 600°C, at which temperature γ-alumina is formed. Yoldas et al. studied calcium aluminate glass and suggested that the pentahedrally coordinated aluminum (AlV) may be strongly correlated with the occurrence of luminescence. Therefore, 27Al NMR analysis was performed to characterize such complexes. Figure 4 shows the 27Al MAS NMR spectra of these samples as a function of the annealing temperature. Besides the resonance lines attributable to tetrahedrally (AlIV) and octahedrally (AlV) coordinated aluminum, a line corresponding to pentahedrally (AlVI) coordinated aluminum has also been observed. It was found that the concentration of pentahedrally coordinated (AlVI) aluminum is dependent on the thermochemical environment within the samples. Furthermore, the AlIV signal increases with the firing temperature, reaches a maximum intensity at about 600°C, and then decreases at a higher temperature in both O2 and N2 annealing atmospheres. When comparing Fig. 3b, it was noted that, although the concentration of pentahedrally coordinated aluminum is higher at 600°C, the relative peak intensity (Ip/IUV) of the O2-annealed nanocables is decreased. This may imply that with the increase of annealing temperature, the OH bond in the pseudoboehmite structure tends to be broken and produce more pentahedrally coordinated aluminum and singly ionized oxygen vacancies (F center). Therefore, in this condition F center decreases, but the pentahedrally coordinated aluminum still exists as indicated from the NMR result.

Because the equilibrium structure during the transformation of boehmite to γ-alumina phase is determined by the number of the OH groups, the surface composition of Al2O3/ZnO nanocables was further examined by XPS for samples annealed at 400°C in N2 and O2 atmospheres as shown in Fig. 5. XPS spectra of Al 2p in annealed Al2O3/ZnO nanocables are shown in Fig. 5a. The peak position for the samples with nearly stoichiometric composition annealed in a N2 atmosphere is located at a binding energy of 74.3 eV, indicating that the Al–O binding state is dominated by the boehmite/γ-alumina phase. In contrast, the Al 2p position of the samples annealed in an O2 atmosphere is located at a binding energy of 74.6 eV, indicating that γ-alumina is easily formed for the sample treated in O2 gas. The asymmetric spectrum of O 1s in Fig. 5b and c contains three peaks at 529.6, 530.8, and (broadly) 532.6 eV. The peaks around 529.6 and 530.8 eV can be assigned to O2− ions in the Zn–O bonds and Al–O bonds, respectively. The peak related to the highest binding energy around 532.6 eV is attributed to OH bonds. As a result, a strong OH–bond peak was observed in a N2 atmo-
Figure 5. (Color online) XPS spectra for the Al2O3/ZnO nanocables of (a) Al 2p and O 1s annealed in (b) N2 and (c) O2 at 400°C.

Conclusion

In summary, we have developed well-aligned arrays of Al2O3/ZnO nanocables on ZnO/Si substrates buffered with a ZnO film by combining a simple chemical solution with a low-temperature treatment. The PL measurement indicates that a strong blue emission peak at ~450 nm appears at 400 and 600°C in O2 and N2 atmospheres, respectively. The phenomenon is strongly related to OH bond cleavage and a phase transition from amorphous to γ-phase alumina, as evidenced by XPS and NMR analyses. The results provide an effective method for constructing nanostructures with a strong blue light emission.

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References