Hydrothermal Synthesis and Properties Postprint of Zinc Oxide Nanorod Arrays

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Abstract

ZnO nanorod arrays were prepared via a hydrothermal method by adding NH4NO3 and Al(NO3)3 to a solution containing dissolved Zn(CH3COO)2 and C6H12N4. The results demonstrate that NH4NO3 added to the solution reduced the defect state density of the prepared ZnO nanorods and decreased the density of non-radiative recombination centers within them. The reduction of non-radiative recombination within the ZnO nanorods led to a 49% decrease in their Stokes shift, thereby yielding high-quality ZnO nanorod arrays. Controlling the addition of NH4NO3 and Al(NO3)3 in the solution enables tuning of the optical bandgap width of the ZnO nanorods within the range of 3.36-3.57 eV. The introduction of Al increased the carrier concentration within the ZnO nanorods, causing the optical bandgap of the nanorods to blue-shift to 3.56-3.57 eV under the Burstein-Moss effect.

Full Text

Hydrothermal Synthesis and Properties of ZnO Nanorod Arrays

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Abstract

ZnO nanorod arrays were synthesized by hydrothermal method from an aqueous solution of $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ with additives of NH_4NO_3 and $Al(NO_3)_3$. The results show that the use of NH_4NO_3 in the solution leads to a decrease in nonradiative recombination centers in the ZnO nanorods by lowering their defect density. The reduction of the nonradiative recombination in ZnO nanorods results in a descent in the Stokes shift of the nanorods by 49%. In addition, the optical band gap of the ZnO nanorods could be adjusted in a range of 3.36–3.57 eV by controlling the additives concentration in the solution.

The increase of the carrier concentration as a result of the Al doping leads to a blue shift of the optical band gap of the ZnO nanorods to 3.56–3.57 eV, which can be ascribed to the Burstein-Moss effect.

Keywords inorganic non-metallic materials, optical band gap, hydrothermal method, nanorods

Introduction

ZnO is a wide-bandgap direct semiconductor with a bandgap of ~3.3 eV and a high exciton binding energy of 60 meV at room temperature. In the field of metal oxide semiconductor research, ZnO has attracted significant attention due to its potential applications. Compared with its thin-film counterparts, ZnO nanorods exhibit lower defect-state density and superior optical quality, making ZnO nanorod-based optoelectronic devices such as thin-film solar cells a hot research topic in recent years.

Currently, the cost-performance ratio of thin-film solar cells still lags behind that of crystalline silicon solar cells. The development goal for next-generation thin-film solar cells is to further improve their conversion efficiency while reducing production costs. This can be achieved by increasing incident photon flux, enhancing light absorption, and improving photogenerated carrier collection. Integrating ZnO nanorod arrays into conventional thin-film solar cell structures can enhance performance through both optical and electrical pathways. Optically, the embedded ZnO nanorods act as light-scattering units that texture the absorber layer, increasing the effective optical path length of incident light within the cell and thereby reducing the required absorber thickness and manufacturing costs. Electrically, the embedded ZnO nanorods position the carrier collection electrodes closer to the photogenerated carrier generation region where collection efficiency is higher, thereby enhancing photogenerated carrier collection, increasing the short-circuit current density, and improving cell conversion efficiency.

For the latter approach, ZnO nanorods serving as carriers and transporters of photogenerated carriers must exhibit minimal non-radiative recombination. Simultaneously, their semiconductor material parameters such as bandgap width and work function must be tunable to control the energy band alignment between the ZnO nanorods and the absorber layer material, ensuring effective collection and transport of photogenerated carriers. Therefore, there is an urgent need to develop new methods for preparing high-quality ZnO nanorod arrays with controllable semiconductor performance parameters and low non-radiative recombination.

The hydrothermal method is one of the common low-temperature solution routes for growing ZnO nanostructures. The Zn source in the solution can come from zinc salts such as $Zn(NO_3)_2$ or $Zn(CH_3COO)_2$, while the O source can come from NaOH or $C_6H_{12}N_4$. The crystal growth process of ZnO nanostructures is susceptible to the influence of additional ions in the solution. In this work, NH_4NO_3

and $Al(NO_3)_3$ were added to a solution of $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ to prepare ZnO nanorod arrays with simultaneously tunable optical bandgap and reduced non-radiative recombination. The effects of NH_4NO_3 and $Al(NO_3)_3$ addition on the properties of ZnO nanorods were analyzed.

1 Experimental Methods

To investigate the effects of NH_4NO_3 and $Al(NO_3)_3$ on the physical properties of the prepared ZnO nanorod arrays, nine samples were prepared using different solution recipes. All samples contained 4 mmol/L $Zn(CH_3COO)_2$ and 4 mmol/L $C_6H_{12}N_4$. For samples 2-5, 20, 40, 60, and 80 mmol/L of NH_4NO_3 were added to the solution, respectively. For samples 6 and 7, 5 and 10 mmol/L of $Al(NO_3)_3$ were added, respectively. For samples 8 and 9, in addition to 40 mmol/L NH_4NO_3, 5 and 10 mmol/L $Al(NO_3)_3$ were added, respectively .

The substrates for growing ZnO nanorod arrays were float glass coated with an Al-doped ZnO film approximately 1000 nm thick. This film was prepared by physical vapor deposition using a sputtering target composed of 97% ZnO and 3% Al_2O_3 (by mass). The distance between the sputtering target gun and the glass substrate was 14 cm, and the substrate rotation speed was 14 r/min. The vacuum chamber of the magnetron sputtering system was evacuated to a base pressure of ~1.2$×10ˆ{-4}$ Pa using a molecular pump. During sputtering, high-purity Ar gas (99.9999%) was introduced into the chamber, and the working pressure was adjusted to 0.12 Pa with an Ar flow rate of 15 mL/min. The glass substrate was not intentionally heated during magnetron sputtering, though its temperature increased slightly due to bombardment by Ar plasma and sputtered material from the target. RF magnetron sputtering was employed at a power of 240 W. To remove contaminated material from the target surface, pre-sputtering was performed for at least 2 min after initiating the RF power source and achieving purple glow, after which the shutters on both the target and glass substrate were opened to begin deposition of the Al-doped ZnO film. A quartz crystal oscillator monitored the film growth process, yielding a deposition rate of 5.6 nm/min. All substrates had cross-sectional dimensions of 1.5 cm × 1.5 cm.

Substrates were sequentially ultrasonically cleaned in acetone, ethanol, and ultrapure water (18.2 $M\Omega \cdot cm$) for 2 min each, then dried with nitrogen before being placed in a stainless-steel hydrothermal reactor with a Teflon liner. The growth time was 5 h at a temperature of 90°C. After growth, the substrates were rinsed with ultrapure water to remove residual salts from the surface.

The surface morphology of the samples was examined using a Nova Nano SEM 450 field-emission scanning electron microscope (SEM) at an operating voltage of 5 kV. To obtain high-quality SEM images, secondary electrons scattered from the sample surface were collected using an in-column secondary electron detector with a working distance of less than 5 mm. The transmittance of the samples was measured using a UV-3600 spectrophotometer with a 15 cm integrating sphere to collect transmitted light. Photoluminescence (PL) measurements were performed to investigate the exciton recombination optical properties in the ZnO nanorods. The PL system used was a LabRAM HR 800 micro-confocal Raman spectrometer with an IK3301R-G He-Cd laser as the excitation source (wavelength 325 nm, power 30 mW). The laser power incident on the sample was attenuated to 1/10 using a filter on the power attenuation wheel. Measurements were conducted at room temperature. The spectrometer focal length was 800 mm, with signal collection exposure time of 1 s and 2 integration cycles. The spectrometer system was calibrated for both wavelength and signal intensity before testing to ensure accurate results.

2 Results and Discussion

Figure 1 [Figure 1: see original paper] shows the transmission spectra of the prepared samples. All samples exhibit high transmittance in the 400–1300 nm wavelength range (solar spectrum-weighted transmittance ~80% without excluding the glass substrate effect), indicating that the prepared ZnO nanorod arrays are suitable as transparent conductive oxide film structures for various solar cell applications. The refractive index of ZnO film in the visible light band is approximately 1.9, differing from air by about 0.9, and the ZnO:Al film substrate used for nanorod growth shows obvious interference fringes in the visible region [11]. After growing ZnO nanorod arrays, the interference fringes in the transmission spectrum of sample 1, prepared from $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ solution, are significantly weakened and nearly disappear. Similar to sample 1, the transmission spectra of samples 2–5, prepared with 20, 40, 60, and 80 mmol/L NH_4NO_3 added to the solution, show no obvious interference fringes. As seen in the SEM images of samples 1 and 3 [Figure 2: see original paper], the discrete columnar structure of the ZnO nanorod arrays results in an effective refractive index of the nanorod array layer lower than 1.9. The nanorod arrays with diameters of approximately 80–100 nm serve as a subwavelength structure that effectively suppresses the appearance of interference fringes across a broad visible light band.

Samples 6 and 7, prepared by adding 5 and 10 mmol/L $Al(NO_3)_3$ to the solution used for sample 1, show interference fringes in the visible band in their transmission spectra. The SEM image of sample 7 [Figure 2c: see original paper] reveals that the ZnO nanorod array density is extremely high, causing the nanorods to pack closely together and form a gapless nanorod film structure. This nanorod film structure leads to interference fringes in the transmission spectra of samples 6 and 7 similar to those observed in sample 1. Sample 9, prepared by adding 40 mmol/L NH_4NO_3 to the solution recipe used for samples 6 and 7, shows no obvious interference fringes in its transmission spectrum. As shown in [Figure 2d: see original paper], the morphology of ZnO nanorods in sample 9 is similar to that of nanorods in samples 1–5. The addition of NH_4NO_3 increases the gap between nanorods compared with samples 6 and 7, thus eliminating interference fringes in the transmission spectrum.

The optical bandgap width of the material can be calculated by linear fitting of $(\alpha h\ )^2$ versus h at the absorption edge, where α is the absorption coefficient, h is Planck' s constant (6.626\$×10^{-34}\$ J•s), and   is the frequency. For direct-bandgap ZnO material, α -lnT (where T is the sample transmittance). Figure 3 [Figure 3: see original paper] shows the $((-\ln T)\times h\ )^2$ versus h plots for samples 1-9. On the low-energy side of the absorption edge, the sample transmittance is approximately 80%, and the deviation from 100% transmittance causes the $((-\ln T)\times h\ )^2$ values to deviate from zero. The optical bandgap width of the ZnO:Al film substrate used for growing ZnO nanorods is 3.65 eV [11], and the optical bandgap widths of samples 1-9 are all smaller than this value. Therefore, the values obtained from fitting the transmission spectra of samples 1-9 correspond to the optical bandgap width of the ZnO nanorods. Table 1 lists the optical bandgap widths of samples 1-9.

Sample 1, prepared from a solution of $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$, has an optical bandgap width of 3.38 eV. The bandgap of sample 2 shows no change compared with sample 1. The bandgaps of samples 3 and 4 redshift to 3.36 eV compared with samples 1 and 2. Sample 5 continues to redshift to 3.35 eV. The bandgap widths of ZnO nanorods in samples 6 and 7 are 3.57 eV and 3.56 eV, respectively, showing a significant blueshift compared with sample 1—190 meV and 180 meV, respectively. This blueshift is likely due to Al doping into the intrinsic ZnO nanorods from $Al(NO_3)_3$ in the solution. The Burstein-Moss effect causes the optical bandgap of Al-doped ZnO nanorods to blueshift by approximately 190 meV compared with undoped intrinsic ZnO nanorod arrays. Al doping raises the Fermi level of ZnO into the conduction band. When the semiconductor absorbs photons, valence electrons transition to the conduction band. Since the conduction band minimum is already filled by the elevated Fermi level, electrons must transition to higher energy levels according to the Pauli exclusion principle, resulting in bandgap broadening in doped ZnO nanorod arrays. The optical bandgap widths of samples 8 and 9 are 3.36 eV and 3.37 eV, respectively, similar to sample 3 and smaller than those of samples 6 and 7. This indicates that NH_4NO_3 suppresses the Al doping process.

In electrochemical deposition of ZnO nanorods, the addition of NH_4NO_3 to the electrolyte promotes Al doping into intrinsic ZnO nanorods and causes bandgap blueshift [11]. Both electrochemical deposition and hydrothermal methods involve heterogeneous nucleation on the substrate surface followed by crystal growth. In both preparation methods, the reaction groups undergo diffusion from the bulk solution to the substrate region, adsorption, surface diffusion and migration, and finally deposition into the crystal lattice. Throughout these four processes, complexation of NH_4^+ and Al^{3+} occurs. The differences between electrochemical deposition and hydrothermal methods include reaction temperature, ion concentration gradient distribution in solution, OH^- generation process, and solution pH. Since Al doping of ZnO nanorods can be achieved by electrochemical deposition within a certain temperature and electrolyte concentration range, while adjusting the hydrothermal reaction temperature and solution concentration still fails to produce Al-doped nanorods, reaction temperature and ion concentration gradient are not the determining factors for the effect of NH_4NO_3 on Al doping.

In the electrochemical deposition process, OH^- (the oxygen source in ZnO) is generated from the reduction of NO_3^- ions in the solution, and OH^- production is limited to the vicinity of the substrate. In the hydrothermal process, OH^- originates from the hydrolysis of $C_6H_{12}N_4$ at high temperature, and OH^- exists throughout the solution. The different OH^- generation methods also lead to differences in solution pH. Therefore, the pH difference between the two preparation methods may cause different complexation processes of NH_4^+ and Al^{3+}. In electrochemical deposition, NH_4NO_3 addition promotes Al doping of ZnO nanorods [11], whereas in the hydrothermal deposition process described here, NH_4NO_3 addition suppresses Al doping of ZnO nanorods.

Figure 4 [Figure 4: see original paper] shows the room-temperature photoluminescence spectra of samples 1-9. All samples exhibit near-band-edge emission intensity greater than defect-state emission intensity in the visible band. In sample 1, prepared from $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ solution, the ratio of near-band-edge emission intensity to defect-state emission intensity is 12. For samples 2–5, this ratio is 25, 30, 21, and 26, respectively. The addition of NH_4NO_3 to the solution significantly increases the ratio of near-band-edge emission to defect-state emission, reduces the defect-state density of the prepared ZnO nanorods, and thus improves optical quality.

The near-band-edge emission peak positions of samples 1–5 are 379.6 nm (3.266 eV), 379.5 nm (3.267 eV), 379.2 nm (3.270 eV), 379.3 nm (3.269 eV), and 379.7 nm (3.265 eV), respectively, showing similar peak positions. The full width at half maximum (FWHM) of the near-band-edge emission peaks for these five samples are 13.8 nm, 13.7 nm, 13.7 nm, 14.7 nm, and 14.5 nm, respectively, indicating that the room-temperature near-band-edge emission mechanism of ZnO nanorods prepared with NH_4NO_3 addition shows no significant difference.

The near-band-edge emission intensity to defect-state emission intensity ratios for samples 6 and 7 are 11 and 12, respectively, similar to sample 1, indicating that the optical quality of ZnO nanorods prepared with $Al(NO_3)_3$ addition is not degraded. The near-band-edge emission peak positions of samples 6 and 7 are 375.6 nm (3.301 eV) and 376.8 nm (3.291 eV), respectively, blueshifting by 4.0 nm (35 meV) and 2.8 nm (24 meV) relative to sample 1. Due to the Burstein-Moss effect, Al doping in samples 6 and 7 broadens the optical bandgap by 190 meV and 180 meV, respectively, causing the near-band-edge emission peaks to blueshift accordingly. The optical bandgap blueshift is greater than the near-band-edge emission blueshift, indicating that bandgap broadening is not the sole cause of the near-band-edge emission shift. Other band structure reconstruction mechanisms are involved during the blueshift process. The FWHM values of the near-band-edge emission peaks for samples 6 and 7 are 17.5 nm and 14.5 nm, respectively. Compared with samples 1–5, sample 7 shows no obvious change in FWHM, while sample 6 exhibits broadening.

The near-band-edge emission intensity to defect-state emission intensity ratios for samples 8 and 9 are 21 and 28, respectively. The optical quality of ZnO nanorods prepared with NH_4NO_3 addition is improved compared with samples 6 and 7, with ratios similar to those of samples 2–5, again confirming that NH_4NO_3 addition reduces defect-state density in the nanorods. The near-band-edge emission peak positions of samples 8 and 9 are 379.6 nm (3.266 eV) and 379.4 nm (3.268 eV), respectively, showing no significant change compared with samples 1–5.

Based on the photoluminescence spectra and the optical bandgap results, the Stokes shift of the samples can be calculated. Sample 1, prepared from $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ solution, has a Stokes shift of 114 meV. Sample 2 shows a Stokes shift of 113 meV, with no obvious change compared with sample 1. Samples 3–5, prepared with 40, 60, and 80 mmol/L NH_4NO_3 added to the solution, exhibit Stokes shifts of 90 meV, 91 meV, and 85 meV, respectively. The addition of NH_4NO_3 reduces the Stokes shift of ZnO nanorods by 24 meV, 23 meV, and 29 meV, respectively, indicating reduced non-radiative recombination inside the ZnO nanorods prepared with 40–80 mmol/L NH_4NO_3. This may result from improved material properties related to electron-phonon coupling, lattice distortion, interface state defects, or point defects [12].

Samples 6 and 7, prepared by adding 5 and 10 mmol/L $Al(NO_3)_3$ to the solution used for sample 1, show Stokes shifts of 269 meV for both. Compared with sample 1 without $Al(NO_3)_3$, the Stokes shift of samples 6 and 7 increases by 136%, indicating that Al doping enhances non-radiative recombination inside ZnO nanorods. This may be due to changes in the internal recombination mechanism caused by incorporated Al, possibly through alterations in electron-phonon coupling, lattice distortion, interface state defects, or point defects [12].

Samples 8 and 9, prepared by adding 40 mmol/L NH_4NO_3 to the solutions used for samples 6 and 7, exhibit Stokes shifts of 94 meV and 102 meV, respectively. The Stokes shift of ZnO nanorods prepared with NH_4NO_3 addition is dramatically reduced compared with samples 6 and 7, with values similar to those of samples 3–5, again confirming that NH_4NO_3 addition reduces non-radiative recombination inside the nanorods.

3 Conclusion

ZnO nanorod arrays were prepared by hydrothermal method with NH_4NO_3 and $Al(NO_3)_3$ added to $Zn(CH_3COO)_2$ and $C_6H_{12}N_4$ solution. Controlling the concentrations of NH_4NO_3 and $Al(NO_3)_3$ enables tuning of the optical bandgap width of ZnO nanorod arrays. Adding NH_4NO_3 to the solution allows tuning of the optical bandgap width in the range of 3.36–3.38 eV. Adding $Al(NO_3)_3$ to the solution increases the carrier concentration in ZnO nanorods through Al doping, resulting in a significant bandgap blueshift to 3.56–3.57 eV due to the Burstein-Moss effect. The addition of NH_4NO_3 reduces the defect-state density of ZnO nanorods, and the resulting decrease in internal non-radiative recombination reduces the Stokes shift by 49%, greatly improving the optical quality of ZnO nanorods.

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