Photoluminescence Studies of ZnO Films Fabricated by Using a Combination of a Hydrothermal Method and Plasma-assisted Molecular Beam Epitaxy Regrowth

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ZnO films were deposited on Si (100) substrates by using a two-step growth process. In the first step, ZnO nanorods were grown by using the hydrothermal method at 140 °C for 5 min. In the second step, a ZnO amorphous layer was deposited on the ZnO nanorods by spin-coating. After completion of the growth process, the films were annealed at 800 °C for 10 min, and a ZnO active layer was deposited on top of the amorphous layer by using plasma-assisted molecular beam epitaxy. Further, temperature-dependent photoluminescence (PL) measurement were conducted to study the optical properties of the prepared films. In the low-temperature PL spectra, emission peaks in the near-band-edge region were observed at 3.370, 3.362, 3.347, 3.329, 3.317, 3.288, 3.263, 3.219, 3.191, and 3.116 eV; these peaks were attributed to free excitons, neutral donor bound excitons, neutral acceptor donor excitons, two electron satellites, and donor acceptor pairs, respectively. These peaks were red-shifted, and their intensity decreased with increasing temperature. The binding energy of the donor was calculated as 43.1 meV by using the Haynes rule. Further, the value α and β, factors in the equation for the energy of localized excitons of donors and acceptors were obtained as 0.73 meV and 750 K, respectively, by fitting the free exciton (FX) peak according to Varshni’s equation. The full width at half-maximum of PL for the films was about 95.1 meV at room temperature; moreover, the following values were obtained for the films by using theoretical equations: the background impurity broadening, Γ₀ = 62 meV, the parameter describing exciton-LO phonon interaction, ΓₐLO = 80 meV, LO phonon energy, ℏωLO = 72 meV, and, the coupling strength of an exciton-acoustic phonon interaction, γₚh = 0.087 meV/K Furthermore, the activation energy was about 60.1 meV.

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I. INTRODUCTION

Recently, ZnO has received significant attention as a compound semiconductor material of II-VI group elements owing to its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature (300 K) [1]. ZnO films can be deposited by using various methods such as sputtering [2], thermal evaporation [3], spin-coating [4], metal-organic chemical vapor deposition [5], and plasma-assisted molecular beam epitaxy (PA-MBE) [6]. Among these growth methods, PA-MBE has the advantages of low defect density and fine growth of films. This is because PA-MBE is carried out under ultra-high vacuum and allows the control of monolayer unit growth. The microstructure of the grown films, their grain size, surface morphology, crystalline density, and orientation, has a significant effect on their physical properties [7]. A number of studies are currently underway to investigate the suitability of ZnO for a variety of applications, such as solar cells [8], blue light-emitting diodes [9], ultraviolet laser diodes [10], photo detectors [11], and piezoelectric and optoelectronic devices [12]. For ZnO-based applications, high-quality ZnO films with
high luminescence efficiency and low defect density necessary. However, the growth of ZnO films on Si substrates is limited owing to the large difference between the lattice constants of ZnO and Si. Several studies have been conducted to improve the quality of ZnO films by various means, such as buffer layers grown at low temperature [13], double buffer layers [14], annealing of ZnO layers [15] and interruption growth method [16].

In this research, we studied the effect of various structure of a ZnO buffer layer, as well as the effect of the regrowth of this layer. ZnO films were grown by using a combination of the hydrothermal method and PA-MBE regrowth. Further, the optical properties of these films were studied by using temperature-dependent photoluminescence (PL) measurements conducted with a He-Cd laser (325 nm) over a wide temperature range of 12-300 K.

II. EXPERIMENTAL PROCEDURE

In this experiment, four samples were prepared as shown in Fig. 1. ZnO films were deposited on p-type Si (100) substrates by spin-coating and PA-MBE, and ZnO nanorods were grown by using the hydrothermal method. The PA-MBE apparatus was equipped with a Zn effusion cell and an oxygen plasma cell. Elemental Zn and O\(_2\) gases, both with a purity of 6 N, were used as the group II and VI sources, respectively. The Si (100) substrate was first cleaned in a piranha solution [H\(_2\)SO\(_4\):H\(_2\)O\(_2\) = 4:1] for 15 min and then in hydrofluoric acid [HF (50%):H\(_2\)O = 1:9] for 5 min. Sample A was composed of three layers: a Zn exposure layer, a ZnO buffer layer, and a ZnO active layer. The initial Zn exposure layers were grown at a temperature of 350 °C to prevent the oxidation of the Si substrate by the O\(_2\) plasma source. The ZnO buffer layer was grown for 20 min at a substrate temperature of 350 °C. The ZnO active layer was grown for 80 min at a substrate temperature of 700 °C. The radio-frequency plasma power (300 W) and O\(_2\) flow rate (3 sccm) were kept constant during sample preparation. In the case of sample B, the ZnO nanorods were grown by using the hydrothermal method at 140 °C for 5 min; the nanorods were grown on the ZnO thin film by sol-gel spin-coating at 2000 rpm for 20 s. The solutions used in the hydrothermal method were prepared by mixing zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\)·6H\(_2\)O) and hexamethylenetetramine (C\(_6\)H\(_12\)N\(_4\)) at a concentration of 0.1 M. Further, the sol-gel solutions were prepared by mixing zinc acetate dehydrate (Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O), 2-methoxyethanol (C\(_3\)H\(_8\)O\(_2\)), and monoethanolamine (C\(_2\)H\(_7\)NO) at a concentration of 0.5 M. Sample C was prepared by adding a ZnO active layer on top of the sample B structure. For this, the ZnO active layer was deposited at 700 °C for 80 min by using PA-MBE. Finally, sample D was prepared by adding a ZnO amorphous layer on top of the sample B structure by sol-gel spin-coating. This intermediate structure was then annealed at 800 °C for 10 min. A ZnO active layer was then deposited on top of this structure at 700 °C for 80 min by using PA-MBE.

The luminescence properties of the prepared ZnO films were investigated by using PL measurements conducted with a He-Cd laser over a wide temperature range of 12-300 K. The laser had an excitation power of 20 mW and was equipped with a 0.75-m single-grating monochromator with a photomultiplier tube.

III. RESULTS AND DISCUSSION

Figure 2 shows the PL spectra of the samples at room temperature. The spectra show a strong UV peak and a weak visible band. The strong UV peak corresponds to the near-band-edge (NBE) emissions that originate from the recombination of the free excitons of ZnO. The weak visible peak corresponds to the deep-level (DL) emissions that originate from various structure defects.

In the spectrum for sample B, the yellow emission peak around 2.15 eV is caused by surface defects in the nanorods [17]; however, the spectra for other samples show blue-green emission peaks around 2.5 eV due to oxygen vacancy defects [17,18]. However, after annealing, these peaks were reduced [17,19]. The inset image in Fig. 2 indicates the I\(_{NBE}/I_{DL}\) values for each sample. The I\(_{NBE}/I_{DL}\) value for sample D is larger than that for sample A. Both samples C and D have a nanorod layer and an active layer. However, the I\(_{NBE}/I_{DL}\) value for sample D is about three times that of sample C. This