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Two-Step Growth of ZnO Films on Silicon by Atomic Layer Deposition

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Abstract–Two-step growth of ZnO by atomic layer deposition at low temperatures was performed to grow quality ZnO films on silicon substrates: first, the growth of a buffer layer at 130 °C and second, the growth of the main layer at 210 °C. Structural and optical properties of the ZnO films deposited on ZnO-buffer/Si(111) were investigated as a function of buffer layer thickness. The films showed a strong UV emission at 380 nm and a weak green emission at 520-570 nm. The ZnO films deposited on a 327 Å buffer layer showed overall the best surface morphology and structural and optical properties.

Key words: ZnO, Two-Step Growth, Buffer Layer, Atomic Layer Deposition, Si Substrate

INTRODUCTION

Zinc oxide (ZnO) is one of the most attractive materials for optoelectronic devices because it has a wide and direct band gap of 3.37 eV and a high exciton binding energy of 60 meV, which is much larger than GaN (28 meV) and ZnSe (19 meV) [Nakamura et al., 2002; Tamargo, 2002]. Furthermore, ZnO films can be grown at a lower temperature than GaN. Hence, the ZnO has received much attention as a candidate material for optoelectronic devices such as ultraviolet (UV) or blue light emitting diodes (LEDs) and laser diodes (LDs) [Kim et al., 2004; Nakamura et al., 2002]. However, it has been reported that the emission properties of ZnO are strongly dependent on the growth techniques such as molecular beam epitaxy (MBE) [Ko et al., 2002; Ohgaki et al., 2002], metal organic chemical vapor deposition (MOCVD) [Ogata et al., 2002; Ye et al., 2002], and radio frequency (RF) magnetron sputtering [Jeong et al., 2004; Ruthe et al., 2004]. In most cases, the ZnO grown on highly mismatched substrates showed a strong emission in the visible region with higher intensity than the UV emission. The origin of the visible emission has been reported due to intrinsic defects such as vacancies of oxygen and zinc, oxygen and zinc interstitials, and antisite defect O_{Zn} [Vanheusden et al., 1996; Lin et al., 2001; Jeong et al., 2004], but it is not yet well understood and still debatable.

Recently, to overcome the defect-related problems and grow high quality ZnO films on mismatched substrates, several research groups have used a buffer layer such as GaN, MgO and ZnS [Nahhas et al., 2001; Chen et al., 2000; Ashrafi et al., 2000]. However, using the hetero-buffer layer results in the diffusion of atoms and degrades the quality of the over-layered ZnO. In order to avoid this problem, several research groups have used a homo-buffer layer on sapphire substrates grown by MOCVD and magnetron sputtering at low temperatures and obtained enhanced structural and optical properties temperature [Ogata et al., 2002; Jeong et al., 2004].

To utilize the ZnO film for large-scale optoelectronic devices, it is required to grow ZnO on silicon substrates. Several research groups have reported the growth of ZnO films on Si substrates using MBE [Iwata et al., 2000], MOCVD [Ogata et al., 2002], and sputtering technique [Jeong et al., 2004; Lin et al., 2001]. However, little work has been reported on the ZnO films on ZnO-buffer/Si substrates using an atomic layer deposition technique (ALD), in which high quality film can be obtained with high-precision thickness control and excellent uniformity at a low temperature [Lim et al., 2000].

In this paper, we report the ZnO films grown on ZnO-buffer/Si (111) by the ALD technique. The silicon substrate has a large lattice and thermal mismatch and a crystalline structure different from ZnO. In order to overcome these limitations, we have examined a two-step growth technique: first, growth of buffer-layer ZnO and second, growth of main-layer ZnO. The ZnO films grown at a low temperature are discussed in terms of structural and optical properties.

EXPERIMENTAL

The growth of main and buffer layers of ZnO films on Si(111) was carried out in an ALD chamber using high purity DEZn and oxygen (99.999%) as zinc and oxygen sources, respectively. Argon (99.999%) was used both as a carrier and purging gas. Typical pulse lengths were 5 seconds for the reactant and 12 seconds for the purge between the reactants, which were all determined from an optimized process window. A two-step growth was performed: first, the growth of buffer layer at 130 °C and second, the growth of main layer at 210 °C. Especially, the effect of buffer layer thickness on properties of the ZnO homo-epitaxy on Si(111) was examined. Crystallinity and orientation of the as-grown ZnO films were investigated by X-ray diffraction (XRD). Optical properties were examined by photoluminescence (PL) spectra at room temperature taken under the excitation by an He-Cd laser (325 nm, 50 mW). Surface morphologies were observed by scanning electron microscope (SEM) and atomic force microscope (AFM).

RESULTS AND DISCUSSION

Fig. 1 shows (a) the thickness of buffer layer ZnO and (b) the growth rate as a function of number of cycles (N_c). The film thick-

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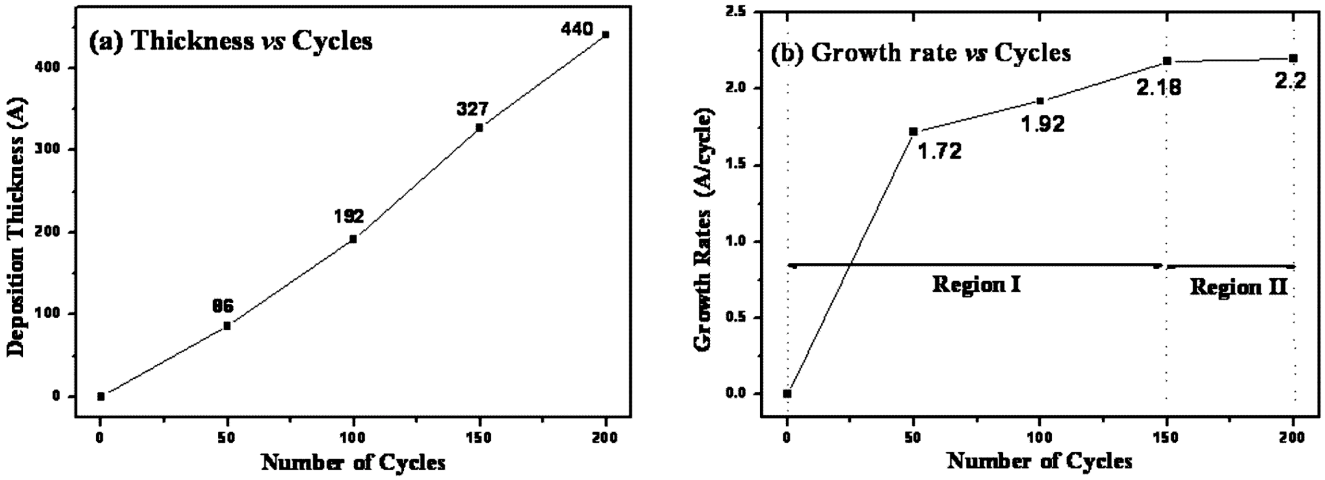

Fig. 1. Thickness and growth rate of ZnO buffer layer on Si(111) as a function of number of cycles.

ness linearly increased with the number of cycles, representing a typical characteristic of the ALD. It is interesting to see that in spite of the linearity of the thickness with N_c, the growth rate (Å/cycle) shows two regions: a transient region where the growth rate increases with N_c (Region I) and a saturated region where the growth rate remains almost constant (Region II). This result indicates that when the desired film thickness is less than about 20 nm, the assumption of linear growth rate leads to an error in estimating the film thickness.

The buffer layer was grown with variation in thickness to examine its effect on structural and optical properties of the as-grown ZnO films on the ZnO-buffer/Si. Figs. 2 and 3 show SEM images of the surface morphology and the cross-sectional view of ZnO/ZnO-buffer/Si(111), respectively, with different buffer layer thicknesses (θ_b). Inset figures in Fig. 3 are AFM images of the surfaces of the buffer layers, having different thicknesses of 86, 192, 327, and 440 Å. It shows that the surface morphologies of ZnO films on ZnO buffers with θ_b=86, 192, and 440 Å were rough (Fig. 2(a), (b) and (d)) and showed columnar structures (Fig. 3(a), (b) and (d)). The rough and columnar structures with θ_b=86 and 192 Å are attributed to the growth mode of a three-dimensional island [Bang et al., 2003; Zhang et al., 2004]. Since ZnO crystal naturally tends to grow as long hexagonal rods along the c-axis direction, the ZnO film structure consists of columnar grains standing perpendicular to the substrate [Puchert et al., 1996]. By contrast, as the θ_b increased further (i.e., 327-440 Å), flat and smooth surfaces of the buffer layers were obtained due to the coalescence of islands [Hiramatsu et al., 1991].

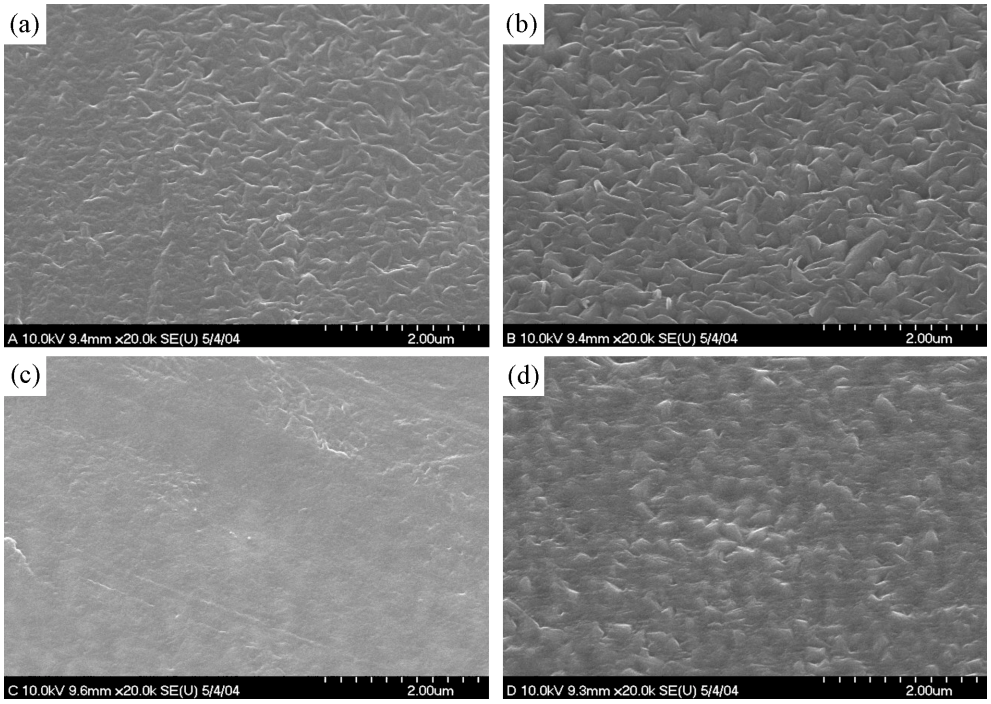

Fig. 2. SEM images of the ZnO film surface grown on ZnO-buffer/Si(111) with different buffer layer thicknesses: (a) 86 Å, (b) 192 Å, (c) 327 Å, and (d) 440 Å.

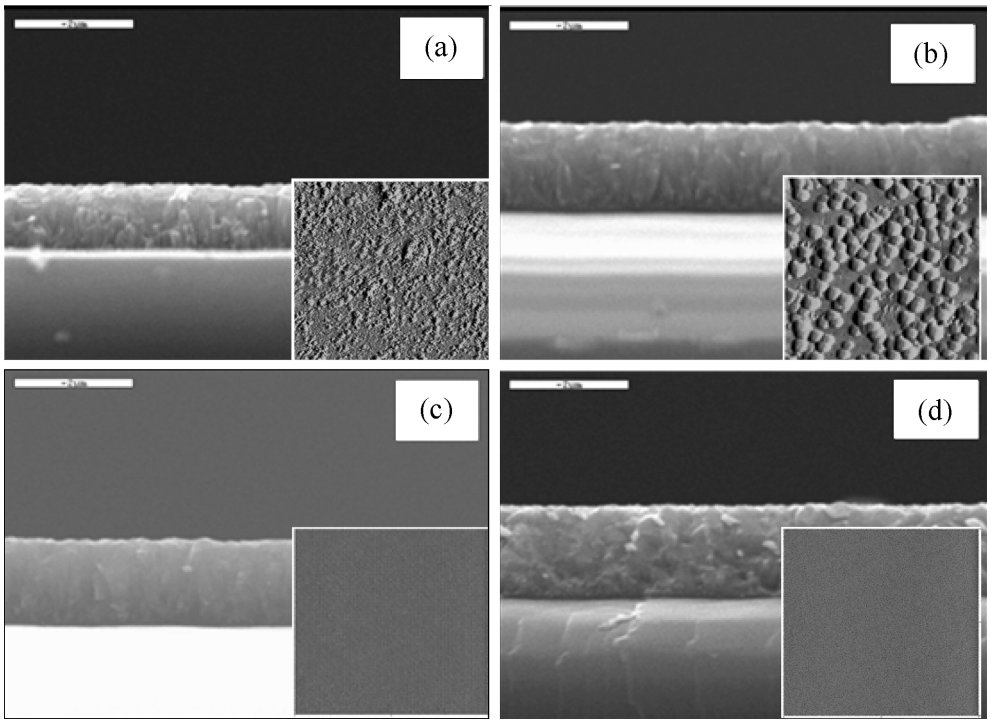

Fig. 3. Cross-sectional SEM images of the ZnO films grown on ZnO-buffer/Si(111) with different buffer layer thicknesses: (a) 86 Å, (b) 192 Å, (c) 327 Å, and (d) 440 Å. Inset figures are AFM images of ZnO buffer layer having different thicknesses.

The main layer ZnO grown with θ_b=327 Å showed overall the best surface and cross-sectional structure (Figs. 2(c) and 3(c)). It is also interesting to see that ZnO film showed a rough and rugged surface again at θ_b=440 Å, which might be attributed to a decrease in nucleation density of ZnO nuclei with thicker buffer layers [Bang et al., 2003; Hiramatsu et al., 1991].

Fig. 4 shows the effect of buffer-layer thickness on the XRD patterns of the ZnO films grown on ZnO buffer/Si(111) with different buffer layer thicknesses of 0 (a), 86 (b), 192 (c), 327 (d), and 440 Å (e). The inset illustrates the dependence of full widths at half maximum (FWHM) of ZnO (0002) peak on the buffer-layer thickness. The films showed a polycrystalline nature, i.e., (1000), (0002), (1010), (1020), and (1100) peaks. When θ_b is greater than 192 Å, the ZnO (0002) peak at 2θ=34.7° arising from hexagonal wurtzite structure is predominant, showing an increase in peak intensity with an increase in the buffer layer thickness. The ZnO film with θ_b=327 Å showed the strongest intensity of (0002) peak (or FWHM value of 0.312°) with suppressing other peaks, indicating a good crystalline quality (see Fig. 4(d)). However, for the films with θ_b=0-192 Å the (0002) peak intensity is relatively low, implying a degradation of the crystallinity caused by the decrease of nucleation density of ZnO nuclei [Zhang et al., 2004].

In order to investigate the optical properties of ZnO films depos-

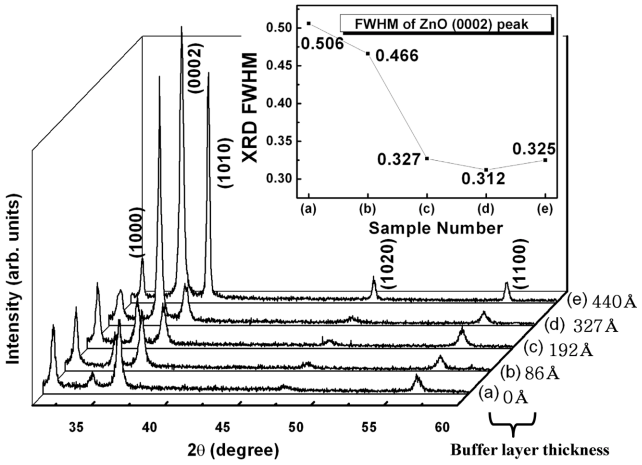

Fig. 4. XRD patterns of the ZnO films grown on ZnO-buffer/Si (111) with different buffer layer thicknesses.

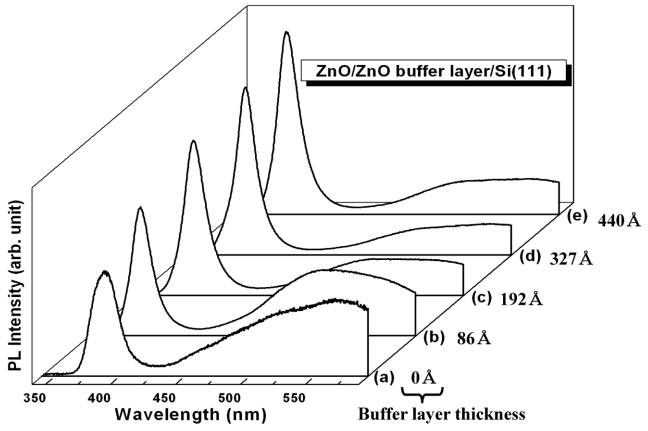

Fig. 5. PL spectra of the ZnO films grown on ZnO-buffer/Si(111) with different buffer layer thicknesses.

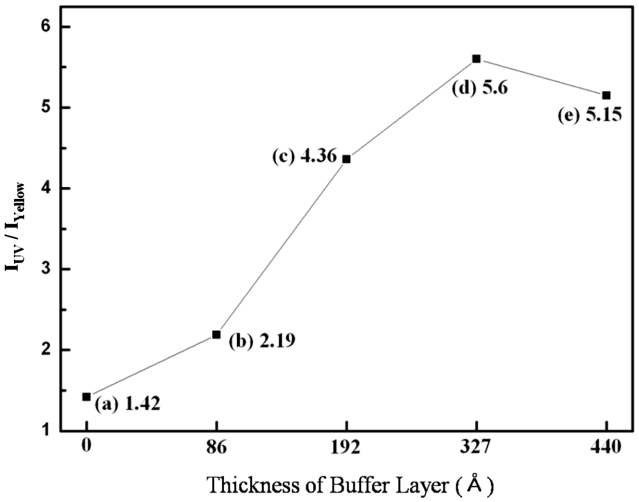

Fig. 6. The intensity ratio of the UV band to the visible band as a function of buffer layer thickness.

ited on ZnO buffer layer with different thicknesses, we measured photoluminescence properties at room temperature using an He-Cd laser with an excitation wavelength of 325 nm. Fig. 5 shows PL spectra with typical emissions in ultraviolet (UV) and visible ranges. In the UV range, near band edge emission at 380 nm is generated by the free-exciton recombination, but in the visible range, deep-level or trap-state emission at 520-570 nm is caused by impurities and structural defects such as oxygen vacancies and interstitials of zinc. The intensity of the UV emission increases with buffer layer thickness, but the deep-level emission is suppressed, indicating that optical properties of ZnO films are affected by buffer layer thickness. Fig. 6 shows the intensity ratio of the UV band to the visible band as a function of buffer layer thickness. The ZnO film with θ_b=327 Å shows the largest intensity ratio. This is because this film has less structural defects and better crystalline structure than others, which are supported by XRD and SEM analysis as shown in Figs. 2-4.

SUMMARY AND CONCLUSIONS

ZnO films were grown on ZnO-buffer/Si(111) with different thickness of the buffer by atomic layer deposition at low temperatures. A two-step growth technique was proposed: first, growth of buffer-layer ZnO at 130 °C, and second, growth of main-layer ZnO at 210 °C. The average growth rate was about 2.2 Å/cycle, and a transient region was observed at the initial stage of ALD. Structural and optical properties were dependent on the buffer layer thickness. The ZnO films deposited on a 327 Å buffer layer showed overall the best surface morphology, structural and optical properties. In conclusion, although we proposed an ALD technique to grow quality ZnO films on silicon substrates with ZnO homo-buffer layers, a further study is needed to improve the optical properties of the ZnO films on silicon substrates for optoelectronic devices application.

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