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Growth of zinc oxide thin films on Y_2O_3/Si substrates by chemical vapor deposition

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Abstract

Epitaxial ZnO was deposited on Si(1 1 1) substrate by atmospheric pressure metal-organic chemical vapor deposition (MOCVD) at 500 °C. A Y_2O_3 buffer layer in epitaxy with Si substrate has successfully suppressed the Si oxidation before ZnO deposition. The Y_2O_3 film was grown by pulsed laser deposition (PLD) on Si(1 1 1) substrate at 800 °C. Also, ZnO was deposited by PLD for comparison with MOCVD. X-ray diffraction and cross-sectional transmission electron microscopy was used to characterize microstructures of the ZnO films and their interfaces with Y_2O_3. The result shows ZnO(0 0 0 2) parallel to Y_2O_3(1 1 1). With the increase of the deposition time, the grain morphology of ZnO thin films evolved from flat structure to columnar structure. Most of the columnar ZnO grains are *c*-axis oriented perpendicular to the interface.

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1. Introduction

ZnO has a wide-direct band gap of 3.37 eV with a high exciton binding energy of 60 meV. Therefore, it is a very attractive material for light-emitting devices in the region of near ultraviolet. As high-quality epitaxial thin films are needed for device development, many ZnO growth techniques such as sputtering [1], pulsed laser deposition (PLD) [2], metal-organic chemical vapor deposition (MOCVD) [3], and molecular beam epitaxy (MBE) [4] have been attempted in past years. MOCVD is particularly attractive for large area development with a high growth rate. Among various substrates for deposition of ZnO thin films such as sapphire (Al_2O_3) [5], GaN [6], and Si [7], Si substrates are easily available in large-area wafers with low cost. However, to grow ZnO in epitaxy

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with Si, one usually encounters the problem of formation of amorphous SiO_2 before ZnO due to the lower formation energy of SiO_2. In the past, a buffer layer such as CaF_2 [8] and ZnO [9] on Si has been used to overcome such a situation. In this work, we use Y_2O_3 as a buffer layer which has several advantages from the point of view of small lattice mismatch (the lattice constant of cubic Y_2O_3 and Si is 10.604 and 5.43 Å, respectively) and more thermodynamic stability. As the lattice mismatch of Y_2O_3(2 2 2) with Si(1 1 1) can be about 2.4%, it has been demonstrated that Y_2O_3 can easily form in epitaxy on Si [10,11]. Here, we report the results of ZnO deposition by MOCVD on Si(1 1 1) using Y_2O_3 as the buffer layer. It has been reported that ZnO films with good crystallinity and orientation were grown by PLD on Si(0 0 1) substrates at 600 °C in a low oxygen pressure [12]. Here, we also report the results of ZnO deposited by PLD which has been evaluated for comparison with the MOCVD results.

2. Experimental procedure

The buffer layer of Y_2O_3 in 100 nm thickness was deposited on Si(1 1 1) substrate which was heated to 800 °C by PLD using 248 nm KrF excimer laser. Details of deposition of Y_2O_3 thin films by PLD have been described elsewhere [13]. X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterization have shown that the deposited Y_2O_3 films have epitaxy with Si(1 1 1) substrate with smooth surface [11]. ZnO thin films were deposited on Y_2O_3/Si(1 1 1) substrates by atmospheric pressure MOCVD and PLD. ZnO thin films were deposited on Y_2O_3/Si(1 1 1) by MOCVD using zinc acetylacetonate ($Zn(C_5H_7O_2)_2$) (99.995% purity) and oxygen gas (99.999% purity) as the zinc and oxygen sources, respectively. The substrate and oxygen gas temperature were all kept at 500 °C. $Zn(C_5H_7O_2)_2$ was heated to 134 °C before flowing into the reaction chamber through a preheating tube at 170 °C with carriers gas of N_2 (99.999% purity). Both O_2 and N_2 flow rates were set in the range of 300–500 sccm. Deposition time of ZnO was varied from 10 to 60 min. For PLD deposition of ZnO, it was deposited immediately after deposition of Y_2O_3 thin films using ZnO ceramic target (99.999% purity) and oxygen gas. During PLD deposition of ZnO, the substrate temperature was kept at 500 °C and the oxygen pressure was 1×10^{-3} Torr. A laser density of 2.5–3 J/cm^2 was used with a pulsed rate of 5 Hz. The crystallinity and orientation of the films were characterized by XRD. To investigate the microstructure and interfaces of the films, cross-sectional TEM was carried out.

3. Results and discussion

XRD patterns in Fig. 1 show the strong and sharp peaks of ZnO(0 0 0 2) and Y_2O_3(2 2 2), indicating that high-quality ZnO films in *c*-axis orientation parallel to $Y_2O_3\langle 1 1 1\rangle$ can be obtained by both MOCVD and PLD methods. The full-width at half-maximum (FWHM) of ZnO(0 0 0 2) is about 0.188° by PLD and 0.207° by MOCVD, showing that the ZnO films deposited by these two methods have similar crystallinity.

Figs. 2(a) and (b) show bright-field TEM images of the ZnO layer deposited on Y_2O_3/Si(1 1 1) for 20 and 60 min by MOCVD. It is seen that the

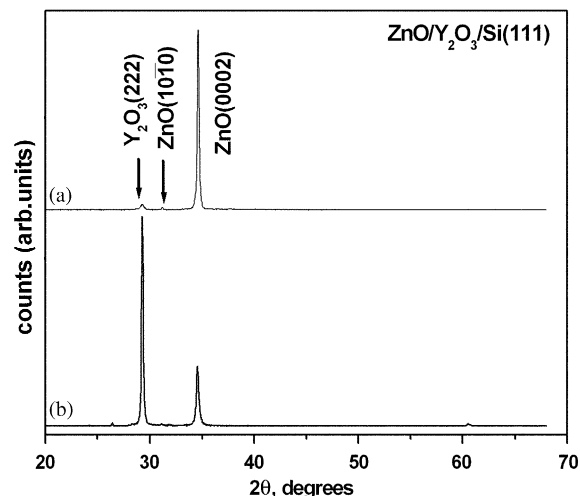

Fig. 1. θ–2θ scan XRD patterns of ZnO deposited on Y_2O_3/Si(1 1 1) substrate by (a) MOCVD for 60 min and (b) PLD.

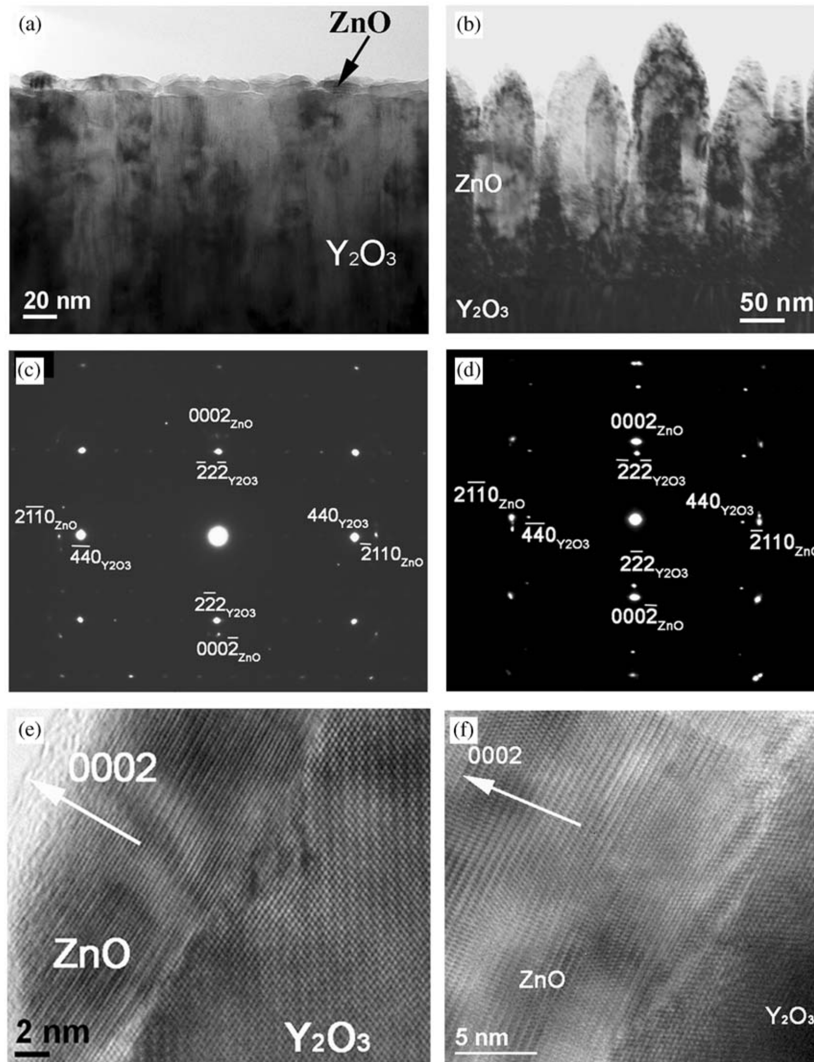

Fig. 2. Bright-field TEM images (a,b), the selected area electron diffraction patterns in [1 1 2] zone axis (c,d), and HR TEM images of the ZnO/Y_2O_3 interface along [0 1 1] zone axis (e,f) from MOCVD samples of deposition time for 20 and 60 min, respectively.

thickness of the ZnO layer is increased from about 10 to 250 nm when the deposition time was extended from 20 to 60 min. This implies that growth rate is nonlinear with deposition time. The probable reason might be attributed to the stability of evaporation of Zn precursor which might result in higher growth rate with time. Further experimental work is in progress to clarify the cause. Interestingly, we found no ZnO deposited on the substrate after 10 min deposition in the same experimental condition, which may suggest that the nucleation barrier on the substrate surface has to be overcome before ZnO formation. For the sample after 20 min deposition, the grains in the ZnO layer are more or less flat in structure with a relatively uniform size of 30 nm in width. However, the grain morphology of the ZnO layer in the sample after 60 min deposition is shown in columnar structure with a lateral dimension in the range of 60–85 nm. Almost all the ZnO grains are

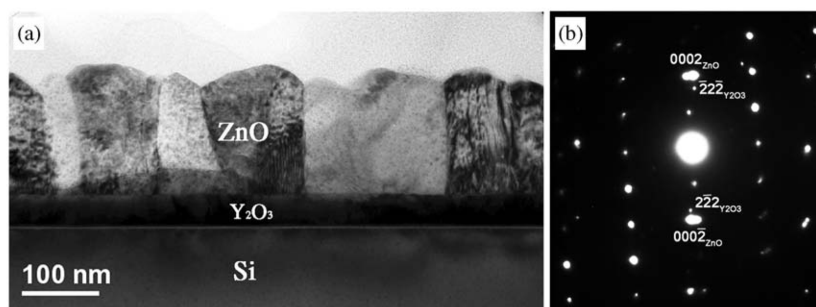

Fig. 3. (a) Bright-field TEM image and (b) the selected area diffraction pattern of ZnO deposited by PLD on Y_2O_3/Si(1 1 1) substrate.

c-axis oriented as shown in the selected area (SAD) patterns in Figs. 2(c) and (d). Hence, the growth rate of ZnO is much faster along the *c*-axis than along the lateral directions. From the flat grain morphology in Fig. 2(a), it is worthwhile to point out that the growth rate in the lateral direction may be instead greater than in the normal direction in the initial stage. From the SAD patterns, the orientation relationship between ZnO and Y_2O_3 can be determined as $\{0\,0\,0\,2\}_{ZnO}||\{2\,2\,2\}_{Y_2O_3}$, $\{1\,1\,\bar{2}\,0\}_{ZnO}||\{4\,4\,0\}_{Y_2O_3}$, $\langle 0\,1\,\bar{1}\,0\rangle_{ZnO}||\langle 1\,1\,2\rangle_{Y_2O_3}$, and $\langle 2\,\bar{1}\,\bar{1}\,0\rangle_{ZnO}||\langle 1\,1\,0\rangle_{Y_2O_3}$. Figs. 2(e) and (f) show HRTEM images of the ZnO/Y_2O_3 interface in films deposited for 20 and 60 min. In both conditions, the ZnO/Y_2O_3 interface is seen to be smooth without the formation of any interlayer. Also, lattice fringes of ZnO(0 0 0 2) plane are parallel to those of Y_2O_3(2 2 2) plane, consistent with the SAD results.

The TEM micrograph in Fig. 3 shows the grain morphology in the ZnO thin film on Y_2O_3/Si(1 1 1) deposited by PLD. It can be seen that the interface between ZnO and Y_2O_3 remains smooth with no formation of any interlayer. The thicknesses of ZnO and Y_2O_3 films are 180 and 40 nm, respectively. The corresponding SAD pattern in Fig. 3(b) shows that most of the ZnO grains are in *c*-axis orientation. However, strong variation of the image contrast in different grains suggests that a large number of ZnO grains are not aligned in the in-plane direction. The ZnO grain size is larger than that deposited by MOCVD as shown in Fig. 2(b). This may be the main cause for the smaller FWHM of ZnO(0 0 0 2) peak in XRD pattern in ZnO film deposited by PLD. Examination of the SAD pattern in Fig. 3(b) shows that there are a number of scattered ZnO(0 0 0 2) and further split (0 0 0 4) reflections, suggesting that some ZnO grains are significantly misoriented away from the surface normal. The XRD pattern in Fig. 1(b) also shows a small peak of ZnO(1 0 $\bar{1}$ 0) resulting from deviated grains. The probable reason may be caused by the high growth rate of 120 nm/min in the present deposition condition as the 180 nm thickness was obtained after about 450 number of laser pulses.

In summary, highly oriented ZnO films with (0 0 0 2) orientation were successfully grown by atmospheric pressure MOCVD on the Y_2O_3/Si(1 1 1) substrates. In the initial stage of growth, ZnO grains have a flat morphology. After long-time deposition, a columnar structure in growth is developed. For PLD deposition with high growth rate, although the ZnO films have good crystallinity, the extent of misorientation away from the *c*-axis increases.

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