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Growth of high-quality epitaxial ZnO films on (10–10) sapphire by atomic layer deposition with flow-rate interruption method

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ABSTRACT

A novel process in an atomic layer deposition system with "flow-rate interruption" (FRI) was developed to obtain epitaxial ZnO films of high quality. The *m*-plane ZnO thin films were grown on *m*-plane sapphire substrates by atomic layer deposition with FRI or a conventional continuous-flow method at the temperature in the range of 25–260 °C; 200 °C appeared optimal. Measurements of X-ray reflectivity indicated that the thickness of ZnO films with FRI is almost twice than that grown with the continuous-flow method. The structural, optical and electrical properties were investigated with X-ray diffraction (XRD), photoluminescence and Hall measurements. The diffraction results indicated that the interrupted flow might extend the reaction of diethylzinc and water through an increased duration to improve the crystallographic quality of the films. According to the results from XRD at high resolution, to substantiate the epitaxial relation between the thin film and the substrate, an off-normal azimuthal scan along ZnO (201) demonstrated two-fold symmetry that indicated the ZnO films to be in epitaxial growth on sapphire. The photoluminescence results showed a strongly enhanced near-band-edge emission of an FRI sample, and the donor–bond exciton appearing in films also indicated superior crystalline qualities. The Hall mobility of the FRI method was up to 64.7 $cm^2 V^{-1} s^{-1}$. The FRI method evidently improved the structural, optical and electrical properties of the ZnO films with small consumption of precursors.

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1. Introduction

ZnO is an attractive material for many applications because of its direct band gap and large binding energy (60 meV) of its excitons [1], larger than for GaN (26 meV) [2] and thermal energy(~25 meV) near 300 K; these properties make ZnO a promising candidate for near-UV optoelectronic devices near 300 K. For the development of material science and the realization of optoelectronic applications, ZnO films are grown with various techniques, such as sol–gel method [3], radio-frequency magnetron sputtering [4], pulsed laser deposition (PLD) [5], metal-organic chemical-vapor deposition (MOCVD) [6], molecular-beam epitaxy (MBE) [7] or atomic-layer deposition (ALD) [8]. Some authors observed, however, that ZnO could generate a spontaneous polarization along the *c*-axis direction and internal electric fields in the multi-quantum well (MQW) structures [9]. The internal electric field separates the electrons and holes present after excitation, decreasing the overlap of their respective wave functions and their radiative transitions. The phenomenon was called quantum-confined Stark effect (QCSE) [10] which would have negative effects on the optical and electrical properties of devices. To diminish the polarization effects, several authors proposed to grow ZnO films along semi-polar or non-polar directions, such as in the *a*-plane, *m*-plane and *r*-plane [10–12]. In this work, we deposited ZnO films on *m*-plane sapphire.

Among several deposition techniques, ALD is promising for growth of films because of its several advantages, such as low temperature, accurate and simple control of thickness, capability and uniformity of a large area, satisfactory reproducibility. According to conventional ALD, the precursors are introduced into the growth chamber sequentially, followed by sustained pumping to evacuate the superfluous reactants. This method is generally called 'continuous-flow (CF)' or 'flow-type' ALD [13]. To obtain epitaxial ZnO films of high quality at low temperature, we developed a novel ALD process with flow-rate interruption (FRI) [14]. In the present work, we investigated the influence of growth with the FRI and CF methods on the crystalline structure, and the optical electrical properties of a ZnO thin film grown on *m*-plane sapphire substrates with ALD. To characterize the structure and thickness of the ZnO films, high-resolution X-ray diffraction (HRXRD) and X-ray reflectivity (XRR) were performed. The photoluminescence (PL) was used to investigate the

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Table 1
Growth conditions of ZnO films on *m*-plane sapphire deposited at 25 to 260 °C.

	Pulse time	Stock time	Purge time	Pump time
FRI method				
H_2O	170 ms	20 s	15 s	20 s
DEZn	170 ms	20 s	15 s	20 s
CF method				
H_2O	500 ms	0 s	15 s	20 s
DEZn	500 ms	0 s	15 s	20 s

optical properties whereas the electrical properties were measured with the Hall effect.

2. Experiments

The ZnO films were deposited on *m*-plane (10–10) sapphire substrates with ALD via a novel FRI technique and a conventional CF method. Diethylzinc (DEZn) and DI water were applied as precursors of Zn and O, respectively. The growth conditions of both FRI and CF methods are listed in Table 1. To determine the variation of the thin film deposition rates under different growth temperature and the relationship between the crystalline quality and orientation, the HRXRD and XRR techniques were applied.

The X-ray scattering measurements were performed at the wiggler X-ray beamline BL-17B1 in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. Two pairs of slits between the sample and the detector enabled a typical wave-vector resolution of ~0.001 nm^{-1} in the vertical scattering plane in this experiment.

The PL was measured at 12 K on samples using a He-Cd laser (325 nm, IK3252R-E, Kimmon) for excitation and with a CCD (cooled with liquid nitrogen to 80 K, Spec-10, Princeton Instruments) and a monochromator (0.5 m, SP-2558A, Acton) for detection. The effective resolution in the PL spectrum was 0.02 nm. The Hall effect was measured (NI PXI-1024Q AC system, National Instruments) with a magnetic field 0.68 T.

3. Result and discussion

We first defined the optimal deposition temperature to be 200 °C assessed from the XRD intensity. As can be seen from the inset of Fig. 1, the integrated intensity of the ZnO (200) reflection for both FRI and CF series have maximal intensity at 200 C. Second, to determine the crystalline quality, optical and electrical properties at the same standard thickness, we performed measurements on ZnO films of the same thickness, 240 nm, grown at 200 °C with FRI and CF, determined by measurement of X-ray diffraction, PL and the Hall effect, for thickness 240 nm of ZnO films with FRI during ~1200 ALD cycles and with CF during ~1800 ALD cycles.

The crystallinity of the ZnO thin films grown by ALD on the *m*-plane sapphire with varied substrate temperature were investigated using HRXRD. The values of *H*, *K*, and *L* in this paper are appropriate to an orthorhombic crystal system and are expressed in reciprocal lattice units (r. l. u.) referring to parameters of the sapphire lattice $a = 0.8245$, $b = 0.475$, $c = 1.2993$ nm and the ZnO lattice, $a = 0.5628$, $b = 0.325$, $c = 0.5207$ nm at 25 °C. The reflection signal was measured from a radial scan ($\theta - 2\theta$ scan) along the surface normal of *m*-plane ZnO thin films with a (200) orientation relative to hexagonal ZnO (10–10) at $2\theta = 31.737$. Fig. 1 show the surface normal radial scan HRXRD spectra for ZnO thin films with growth temperature in the range of 25–260 °C by ALD of FRI method and CF method. ZnO thin films in both series were deposited with 100 ALD cycles. The results show that the ZnO (200) signal became a dominant phase for a deposition temperature above 100 °C. The diffraction intensity reflects the crystalline quality and increased with increasing growth temperature up to 200 °C for the FRI method. In addition, the XRD patterns of the FRI method also show distinct tight fringes that became increasingly symmetric both near either side of the (200) signal and extending farther than with the CF method for a growth temperature near 200 °C. This evidence indicates that the ZnO films grown with the FRI method were thicker and flatter than with the CF method. In the inset of Fig. 1, the integrated intensity of the ZnO (200) reflection for both FRI and CF series, indicating that the FRI series had a greatly increased intensity for a growth temperature in the range of 120–260 °C and for both series the optimal temperature is 200 °C.

Fig. 2 shows experimental results of XRR (open circles) and their best fitted results (solid line). The simulation of the specular reflectivity is based on the recursive formalism of Parratt [15] to acquire the physical parameters of the ZnO thin films. With the Mercury code [16] we determined the physical parameters of the films, including roughness and thickness. The growth rates and roughness of the ZnO films calculated from the fitted results of XRR are shown in the inset of Fig. 2, which clearly indicate a greater rate of growth for the FRI method over all the growth range because the stock mode provides a sufficient duration for the precursors to react with the substrate surface in the growth chamber. The growth window with a flat growth curve of the FRI method in the range of 60–220 °C

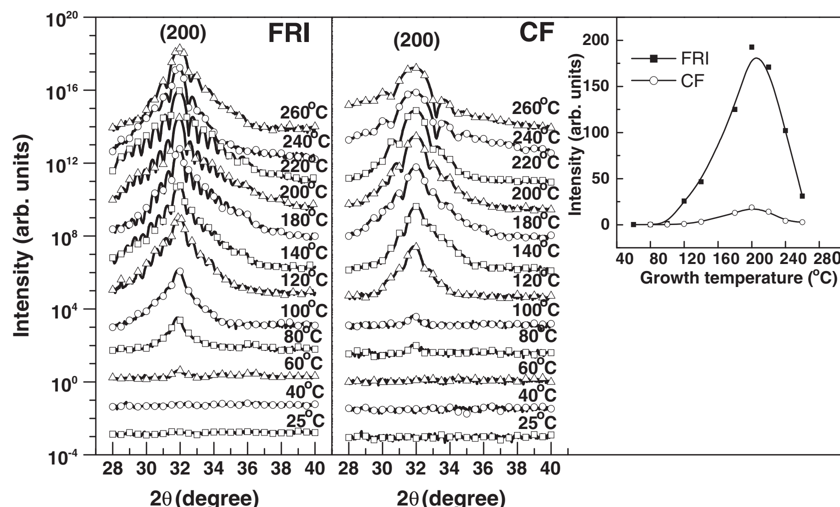

Fig. 1. The surface-normal radial scan XRD spectra for ZnO thin films (100 cycles) with growth temperature in the range of 25–260 °C with FRI and CF methods.

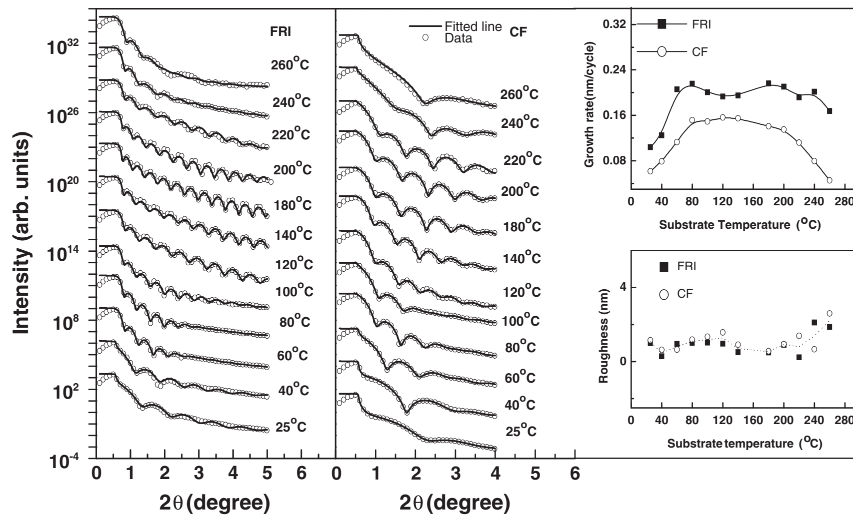

Fig. 2. X-ray reflectivity and their best fitted curves of ZnO films (100 cycles) with growth temperature in the range of 25–260 °C. The inset shows the growth rate and roughness obtained from the fitted results for both of the FRI and CF methods.

seems wider than for the CF method in the range of 80–200 °C. Below 100 °C the growth rate decreased because the thermal energy was insufficient to overcome the potential barrier of the chemical reaction. In contrast, above 200 °C the growth rate decreased at higher temperature because the greater thermal energy induced surface decomposition or desorption. Several authors reported that the growth rate decreased in the temperature range above the growth window with increasing substrate temperature [8,17–19]. The XRR fitting also yields the surface roughness shown in the inset of Fig. 2. The surface roughness obtained from XRR fitting is consistent with AFM measure result (not shown here). The results indicate that ZnO films grown with FRI have smoother surfaces than with CF within the specified range of temperature, in agreement with the distribution of fringes in the FRI ZnO (200) signal shown in Fig. 1.

The FRI method yielded a superior surface roughness for a thick film and satisfactory crystalline quality at 200 °C. To compare the two growth methods in a fair manner, we grew ZnO films of the same thickness and measured the crystalline quality, optical and electrical properties. We compared the ZnO films of the same thickness, 240 nm, grown at 200 °C with FRI with 1200 ALD cycles and CF method with 1800 ALD cycles.

Fig. 3 shows a radial scan along the (*H* 0 0)-direction at the surface normal of ZnO films. The values of *H* depended on parameters of the sapphire lattice $a = 8.245$. There appear three reflection signals, respectively ZnO (200), ZnO (400) and sapphire (600) in Fig. 3, the intensity of the ZnO (200) grown with the FRI method (solid squares) was 3 times that with the CF method (open circles). To examine the behavior of the epitaxial relation between ZnO and sapphire, we introduced an off-normal azimuthal scan as shown in Fig. 4 which exhibits the off-normal azimuthal scan curve of ZnO (110) and (201). The full width at half maximum (FWHM) of the FRI method was 1.272° (broad band) and 0.0211° (narrow band) respectively, which are narrower than 1.513° (broad band) and 0.0246° (narrow band) of the CF method. The film/substrate interface alignment of the FRI method was better than with the CF method; Fig. 4 clearly exhibits a two-fold symmetry between ZnO (201) and sapphire (310). No other feature was observed in the intervals between the two lines, indicating a perfect alignment of *c* and *b*-axes of ZnO unit cells along those of the sapphire substrate. These results provide firm evidence that a strongly epitaxial layer was deposited on the substrate by both methods. The reciprocal space mapping (RSM) results in Fig. 5 and the azimuthal scan of Fig. 4 indicate that an epitaxial relation between ZnO and sapphire follows $[201]_{ZnO}||[310]_{sapphire}$ and $[310]_{ZnO}||[404]_{sapphire}$. Moreover, the broad line of ZnO (201) was also broader than that of ZnO (110). In previous work [20], we obtained the in-plane relation between ZnO and *m*-sapphire follows $[020]_{ZnO}||[006]_{sapphire}$ and $[002]_{ZnO}||[020]_{sapphire}$, and identified a

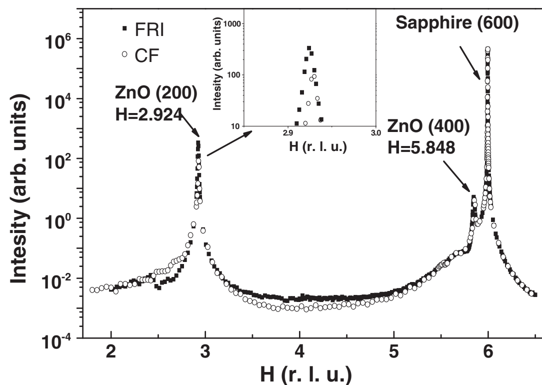

Fig. 3. Radial scan along the surface normal of ZnO films with the FRI and CF methods with the same thickness, 240 nm.

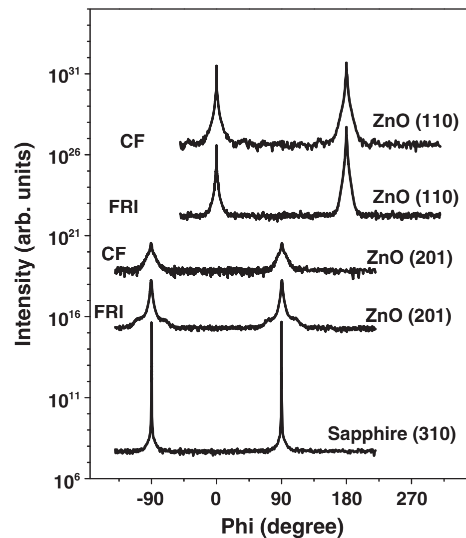

Fig. 4. Azimuthal scans (Φ scan) of the ZnO film peak and the substrate Bragg peak with both methods, including ZnO (110), ZnO (201) and sapphire (310).

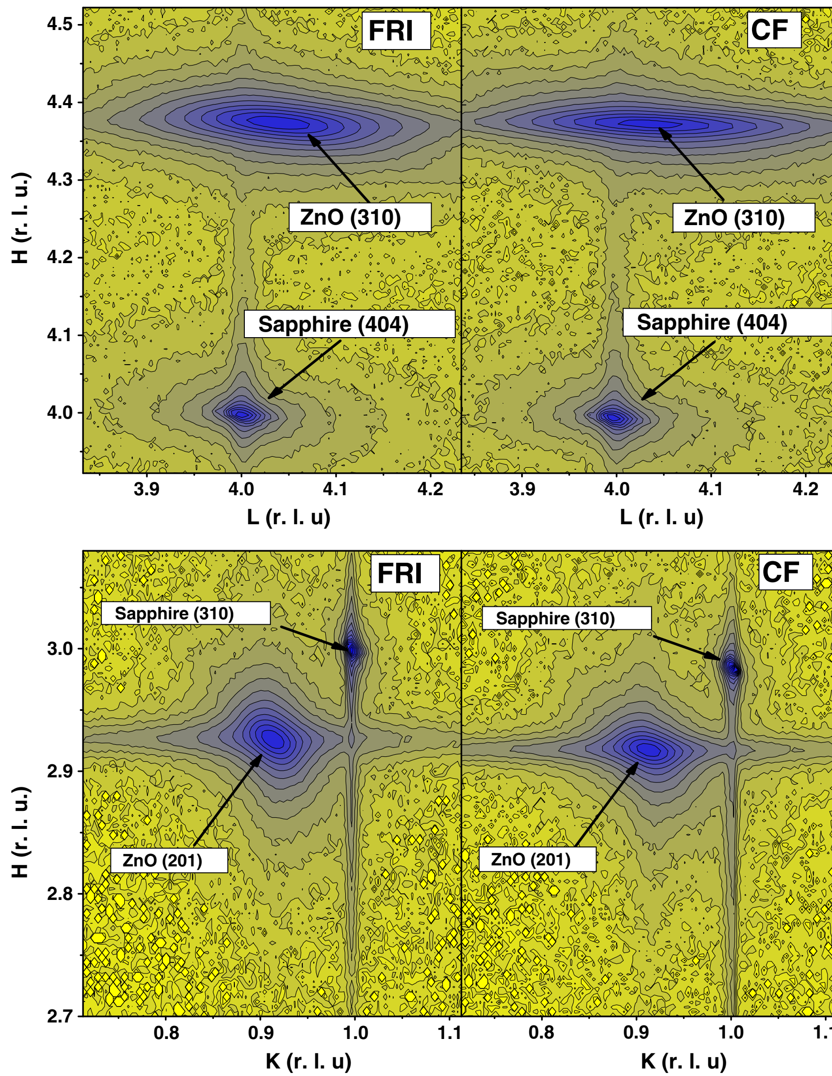

Fig. 5. RSM patterns of ZnO films deposited with FRI and CF methods, including ZnO (310) and sapphire (404), ZnO (201) and sapphire (310).

large lattice mismatch (~9.38%) between sapphire (020) and ZnO (002). It is thus reasonable that the FWHM of ZnO (110) was narrower than for ZnO (201). In Fig. 5, mosaicity results in the elongation of the layer signal along the in-plane direction (*K* and *L*) and were not completely aligned along the normal direction (*H*), indicating almost full relaxation of strain in ZnO films of thickness 240 nm, but the gradient curves of ZnO with the FRI method focused more on ZnO (201) and ZnO (310) points in reciprocal space signify a small lattice distribution and indicate greater crystalline quality. Figs. 4 and 5 show not only that the ZnO films were confirmed to be epitaxial films but also that the FRI method improved the crystalline quality of these ZnO films.

The results of PL measurements are shown in Fig. 6. The films deposited with the FRI method (solid squares) exhibit strong near-band-edge (NBE) emission (D_0X) at 3.364 eV [21]. The films deposited with the FRI method show more intense NBE emission than from the CF method, and also determined that the optical properties of the ZnO films were greatly improved with the FRI method, in agreement with the comparison of crystalline quality. The emission signal near 3.0 eV for ZnO films from the CF method might be contributed by stacking faults [22] to promote the production of accepter states in ZnO films, preferring to recombine between donor and acceptor [23].

Table 2 shows the electrical resistivity, mobility and carrier concentration of ZnO films with the FRI and CF methods measured with

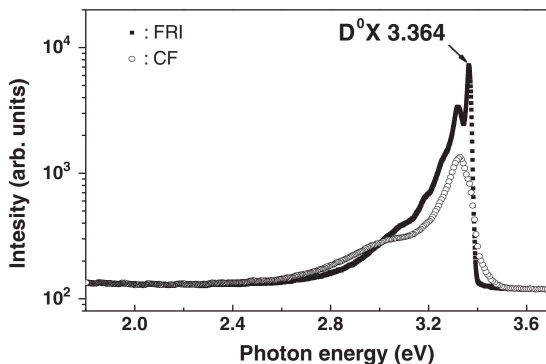

Fig. 6. PL measurements of ZnO films: FRI and CF methods.

Table 2
Mobility, resistivity and carrier concentration obtained from Hall measurements.

	Mobility (cm^2/Vs)	R (/ohm-cm)	Carrier concentration (N/cm^3)
FRI method	64.7 (±0.2)	1.0×10^{-2} (±0.1)	-9.5×10^{18} (±0.2)
CF method	34.8 (±0.3)	2.5×10^{-3} (±0.2)	-6.8×10^{19} (±0.3)

the Hall effect. The growth of films with FRI clearly presents a greater mobility, greater resistivity and smaller carrier concentration than from the CF method. The ZnO films as-grown typically exhibited *n*-type conductivity and a native carrier, attributed to intrinsic defects, such as zinc interstitials and oxygen vacancies [24]. The green–yellow luminescence of ZnO was due to oxygen vacancies in the ZnO crystals [25]. Apart from the intrinsic defects, the absence of green–yellow luminescence in PL spectra and greater electrical resistivity were in agreement with the superior crystalline quality with the FRI method.

4. Conclusion

We investigated the effect of growth temperatures in the range of 25–260 °C on the structure of *m*-plane ZnO on *m*-plane sapphire with FRI and CF methods. Both methods had an optimum temperature at 200 °C. The roughness and growth rate of ZnO films improved with FRI in the range of 60–220 °C of the growth window. The duration of the precursor pulses with the FRI method compared with the CF method indicated that the FRI method can decrease the consumption of precursors. The epitaxial relation of ZnO films of thickness 240 nm on *m*-plane sapphire is confirmed. The FRI method showed a strongly improved crystalline quality, optical properties and electrical mobility of ZnO films.

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