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Epitaxial growth of ZnO films at extremely low temperature by atomic layer deposition with interrupted flow

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ABSTRACT

Thin crystalline films of zinc oxide (ZnO) of high quality have been grown epitaxially on a (0 0 0 1) *c*-plane of a sapphire substrate with atomic layer deposition (ALD) at extra-low temperature. With diethylzinc (DEZn) and deionized water as precursors in combination with interrupted flow, we obtained ZnO thin films with an optimal growth window in a range 25–160 °C, so effectively lowering the growth temperature by about 120 °C relative to the conventional method involving a continuous-flow. We characterized the microstructure of these films with X-ray reflectivity and high-resolution X-ray diffraction (XRD) measurements. The XRD results indicate that the stock time might extend the reaction of DEZn and water through an increased duration. This low temperature for growth results in increased crystalline quality and reduced the non-radiative recombination process to enhance the optical properties of ZnO films.

1. Introduction

Zinc oxide (ZnO) has attracted much attention because of its direct wide band gap, $E_g = 3.4$ eV near 295 K, and large exciton binding energy, ~60 meV [1], which is about three times that of GaN [2]. The doped ZnO is a prospective material for applications such as light-emitting diodes (LED), field-effect transistors (FET), UV lasers operating near 295 K, gas sensors, piezoelectric transducers, transparent electronic circuits, surface-acoustic-wave devices, solar cells, and spintronics [3–10]. A requisite for an application in optoelectronics is doping ZnO of both n- and p-types. A great extent of electron doping in nominally undoped ZnO is attributed to the presence of zinc interstitials, oxygen vacancies and hydrogen. Incorporated carbonates and hydrogen carbonates have also been suggested to contribute to the n-type conductivity of ZnO films as grown [11]. These defects, producing heavy n-type doping, introduce shallow donor levels approximately 0.01–0.05 eV below the conduction-band minimum of ZnO [3,4]. ZnO thin films are prepared with various techniques such as the sol–gel method, radio-frequency magnetron sputtering [12,13], pulsed laser deposition [14,15], oxidation of zinc-based materials [16,17], metallorganic chemical-vapor deposition (MOCVD) [18], molecular-beam epitaxy (MBE) [19,20], or atomic layer deposition (ALD) [21–24].

Growing ZnO at a low temperature is crucial to avoid foreign phases in a material doped with a transition metal [25], and such growth makes possible the obtaining of ZnO on flexible or organic substrates. The concentration of free carriers in a ZnO thin film depends strongly on the growth method and the parameters used in that process. The most important factor that influences the electric parameters of a ZnO thin film is the temperature of its growth, as it controls the thermodynamics of that process [26]. Deposition at a high temperature can intensify the formation of oxygen vacancies and so contribute to a high level of n-electron doping. This point has not been explored seriously as most efforts were concentrated on obtaining ZnO films of high structural quality, which requires a high growth temperature. The potential for flexible, light-weight and mechanically strong electronics based on plastic substrates has, however, motivated intensive research on materials that can be grown at a low temperature. Plastic substrates, such as polyethylene terephthalate, limit the processing of a device to 150 °C, which makes silicon-based electronics incompatible with plastic substrates. Organic semiconductors that degrade under normal atmospheric conditions [27] require an application of protective layers. In these circumstances the possibility of low temperature processes makes ZnO an attractive material for transparent thin film transistors (TFT).

Polycrystalline or highly orientated ZnO films can be grown on (0 0 0 1) sapphire substrates using conventional ALD at tempera-

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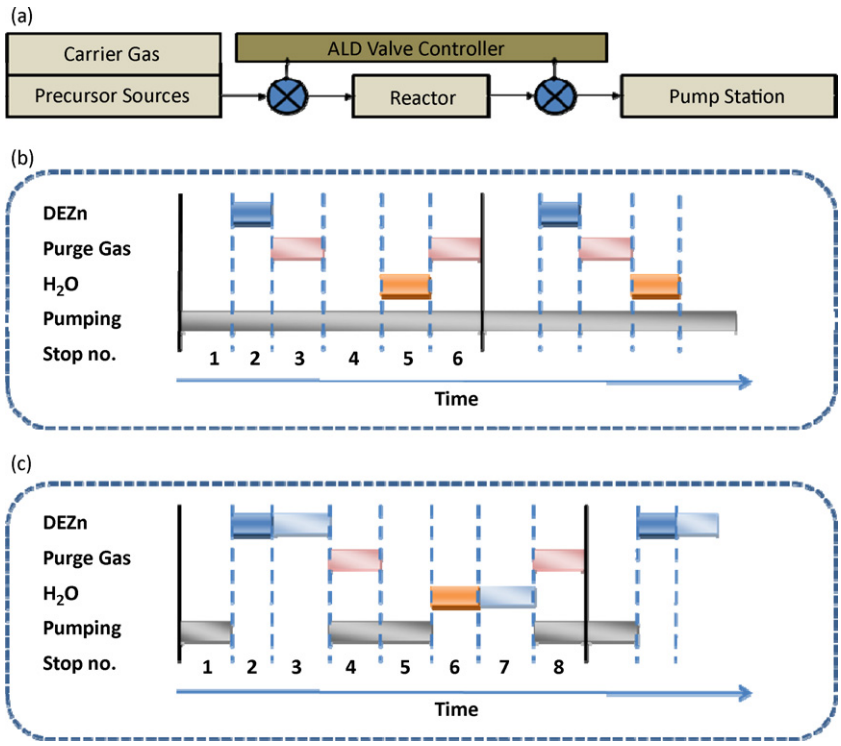

Fig. 1. (a) Schematic diagram of the ALD system. (b) Time table of continuous-flow-type ALD for comparison of *stock mode* with *non-stock mode*. (c) Time table of flow-rate type ALD, stock mode in steps 3 and 7 are stock intervals of the precursors.

tures in a range 70–300 °C [28,29]. ALD involves a self-limiting vapor-phase chemisorption that relies on consecutive surface reactions and utilizes critical purge steps to prevent interactions between reactive precursors [30]. According to conventional ALD, precursors are introduced sequentially into a growth chamber, and cycles of precursor dosing are interrupted by periods of purging with an inert gas such as nitrogen. All processes involve sustained pumping to evacuate superfluous reactants. This method is thus called 'continuous-flow' or 'flow-type' ALD. This ALD is superior at low temperature to other deposition methods, but temperature is also an important factor controlling preferred orientation [31]. This reason might be that the thermal budget is insufficient at very low temperatures. To obtain epitaxial ZnO films of high quality at low temperature, we developed a novel ALD process with flow-rate interruption (FRI) for which we have installed an extra quick ALD diaphragm valve between the reactor and the pump. The valve is closed first before a precursor is introduced into the reactor to retain a precursor in the reactor chamber. The main influences of this step are to enhance the precursor density in the reactor and to extend the duration of reaction at the sample surface; these two effects might increase the rate of reaction at low temperatures. The interval during which a reactant held in the reaction chamber is called the *stock period*. A schematic diagram of the ALD system and a flow-chart comparison between continuous-flow (called *non-stock mode*) and FRI (called *stock mode*) appear in Fig. 1. The main difference between the stock mode (as shown in Fig. 1(c)) and the non-stock mode (Fig. 1(b)) is that pumping is interrupted and *stock* steps are added in the stock mode.

2. Experimental

In this work, the pulse durations of water, 15 ms, and of DEZn, 10 ms, were the same for both growth modes; the stock period was 3 s for both water and DEZn in the stock mode. All other conditions for both modes and precursors were identical. The purge and pumping periods were 10 and 6 s, respectively; the purge pressure was set to 2 torr. All samples were grown with 200 ALD cycles to a total thickness about 50–80 nm.

X-ray diffraction measurements were obtained by a Mac Science M18XHF X-ray powder diffractometer using Cu Kα radiation in the X-ray laboratory at National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The in-plane structure was characterized also on measuring the crystal truncation-rod (CTR) intensity with a synchrotron X-ray source; these synchrotron experiments were performed at wiggler beamline BL-17B1 of NSRRC. Using two pairs of slits between the sample and detector provided a typical wave vector resolution ~0.001 nm^{-1} in the vertical scattering plane in this experiment. For PL measurements near 25 °C, a He–Cd laser (325 nm, IK3252R-E, Kimmon) served as an excitation source and a liquid-nitrogen cooled UV-enhanced CCD (spec-10, Princeton Instruments) as detector after a monochromator (0.5 m, SP-2558A, Acton) with 10 μm entrance slit for 0.02 nm spectrum resolution.

3. Results and discussion

Fig. 2(a) shows XRD patterns measured from a radial scan (θ–2θ scan) along the surface normal of ZnO films grown at varied substrate temperatures. These XRD results display only the ZnO (0 0 2) reflection maximum of the non-stock mode at a low growth temperature, but a (1 0 1) signal appeared when the growth temperature increased above 100 °C. A small thermal budget precludes deposition on sapphire near 25 °C in the non-stock mode. In contrast, ZnO films developed in the stock mode not only had an enhanced (0 0 2) signal but also suppressed the (1 0 1) phase until the growth temperature was greater than 180 °C. The integrated intensity of the ZnO (0 0 2) signal was enhanced in the overall temperature range, increased rapidly from 80 to 40 °C and exhibited a maximum at 40 °C. The intensity in the stock mode was almost 16 times that in the non-stock mode at 40 °C. The stock mode also diminished the full width at half maximum (FWHM) of the (0 0 2) signal as shown in Fig. 2(c). Our results demonstrate clearly that adding a stock period to the growth can improve the crystal quality of the films and enlarge the range of the growth window.

We estimated the size of grains in ZnO thin films according to Scherrer's formula. The size of grains in the ZnO film obtained in the stock mode is approximately ~50 nm, hence near the total thickness of the ZnO film, whereas the size of grains in the non-stock

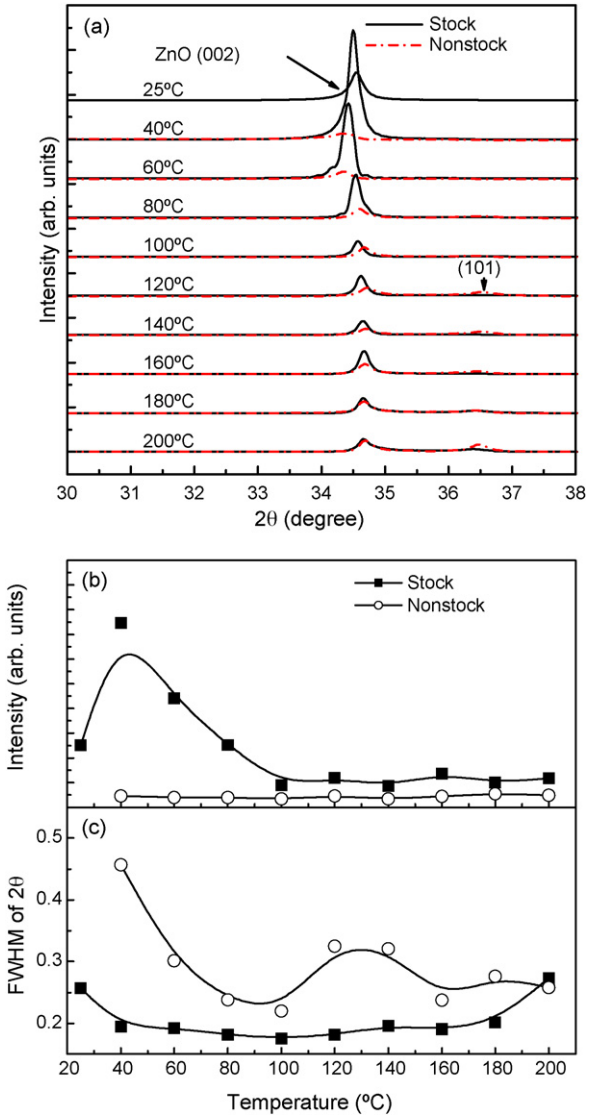

Fig. 2. XRD results for ZnO films deposited at varied substrate temperature: (a) X-ray intensity distribution measured from a radial scan (θ–2θ scan) along the surface normal of ZnO films, (b) integrated intensity of (0 0 2) Bragg signal, and (c) FWHM of (0 0 2) Bragg signal.

mode is ~25 nm. This evidence might explain how the stock mode suppresses the (1 0 1) phase through a single domain from the interface to the film surface. A XRD scan in the normal direction showed that the ZnO $\vec{c}$-axis was well aligned to the substrate surface. We inspected also the off-normal scan to examine the epitaxial relationship between the film and the substrate. Fig. 3 shows a sapphire (1 1 3) scan along the Miller index of reciprocal lattice space and the *x*-axis show in the *h* index of reciprocal lattice units (r.l.u.) referred to the sapphire substrate. A broad feature coexists with a narrow Bragg line, which originates from the sapphire substrate; this broad feature, indicated by arrows in Fig. 3, is ascribed to the ZnO (1 0 1) Bragg signal of the deposited layer, which is confirmed by the variation of relative intensity between the two peaks as a function of angle of X-ray incidence. Azimuthal scans of a deposited film near a ZnO (1 0 1) surface signal and the sapphire (1 1 3) substrate Bragg signal, as shown in the inset of Fig. 3, clearly exhibit sixfold symmetry with the same orientation. No other feature was observed in the intervals between the six signals, indicating an effective alignment of $\vec{a}$ and $\vec{b}$ axes of ZnO unit cells along those of the Al_2O_3 substrate. These results provide not only firm evidence for a strongly epitaxial

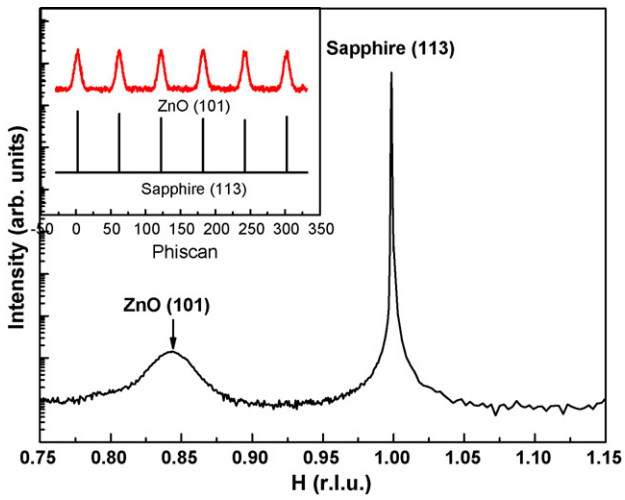

Fig. 3. (1 1 3) off-normal *h k l* scans; inset shows an azimuthal scan (Φ scan) of both sapphire (1 1 3) and ZnO (1 0 1) Bragg signals for a ZnO film grown at 40 °C in the *stock* mode.

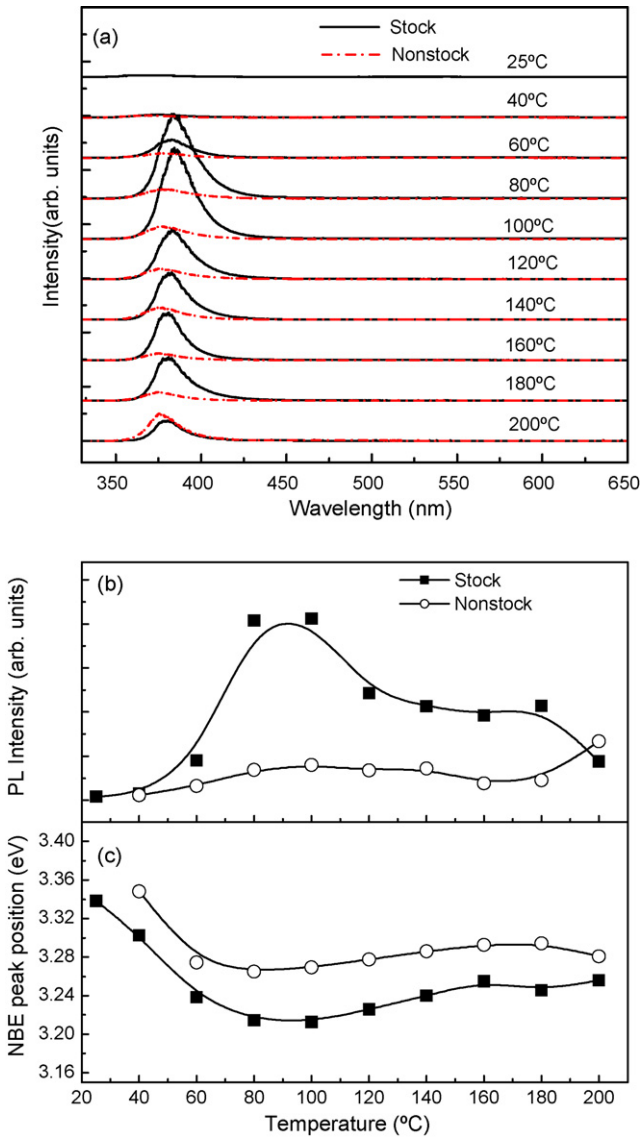

Fig. 4. PL measurements of a ZnO film deposited at varied substrate temperature for (a) PL intensity, (b) integrated near-band-edge emission intensity, and (c) position.

layer having been deposited on the substrate but also the first evidence that effective epitaxial ZnO films can be formed on a (0 0 0 1) *c*-plane sapphire substrate in the ALD region with a FRI method for growth in a temperature range 25–160 °C.

PL tests show that a strong, near-band-edge (NBE) excitonic emission is observed near 25 °C for all investigated ZnO films deposited at various substrate temperatures. Fig. 4(a) shows the PL intensity of a sample in the stock mode that increased appreciably for a growth from 60 to 180 °C relative to a sample in the non-stock mode, with a result summary in Fig. 4(b). The PL spectra of all samples prepared in both stock and non-stock modes show no significant other defect-related emission feature, even though the CCD had adequate quantum efficiency in this region, which demonstrates that the ZnO thin films were satisfactory, in agreement with XRD results. Moreover, the notable promotion of intensity in the stock mode from 25 to 100 °C and the red shift of the NBE position (Fig. 4c) showing an opposite trend might be attributed to an incorporation at a low temperature of hydrogen atoms as a shallow donor to enhance carrier recombination and cause a red shift of NBE [32,33].

4. Conclusion

In summary, we grew ZnO epitaxial films using ALD with the FRI method at 25 °C. The XRD results indicate that the stock time might extend the reaction chain of DEZn and water through an increased duration of reaction and enhance the rate of reaction at a greater pressure in the chamber. The PL results exhibit strong exciton emission enhanced as a small thermal energy might impede self-compensation between Zn and O so as to decrease the density of defects in ZnO thin films.

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