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Growth mode in strained ZnO films on Al_2O_3(0001) during sputtering

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Abstract We investigated the temperature dependence of growth mode in highly mismatched sputter-grown ZnO/Al_2O_3(0001) heteroepitaxial films using real-time synchrotron X-ray scattering. We find that the growth mode changes from 2 dimensional (2D) layer to 3D island in early growth stage with temperature (300°C–500°C). At around 400°C, however, intermediate 2D platelets nucleate in early stage, act as nucleation cores of 3D islands and transform to misaligned state during further growth. The results of the strain evolution during growth suggest that the surface diffusion is a major factor in determining the growth mode in the strained ZnO/Al_2O_3(0001) heteroepitaxy.

Keywords Growth mode · Strain evolution · ZnO · Sputtering

1 Introduction

For wide bandgap semiconductor materials, ZnO has some notable properties of large bond strength and the extreme stability of excitons, offering the prospect of practical lasers with low thresholds, even at high temperatures [1]. But one of the problems is that defects of ZnO films degrade efficient and lasting emission [2]. In connection with this, it is important to obtain high crystalline quality ZnO films in optoelectronic applications.

Many studies have been done on the growth modes of ZnO, which ultimately affect the epitaxial quality. The growth modes were sensitively dependent on the substrate temperature. For instance, ZnO growth mode changed from 3D to 2D with temperature (400°C to 900°C) in molecular beam epitaxy (MBE) [3] or in metal-organic vapor phase epitaxy (MOVPE) [4]. The growth mode with temperature in sputter deposition, in spite of its simplicity and extensive use, is not yet well established [5]. In this article, we present the temperature dependence of the growth mode in early stage in sputter-grown, highly mismatched ZnO/Al_2O_3(0001) heteroepitaxial films using real-time synchrotron X-ray scattering.

2 Experiments

The ZnO films were grown on Al_2O_3(000l) by radio-frequency magnetron sputtering [6]. The working pressure was fixed to 20 mTorr with a mixed gas of Ar-10% O_2. The substrate temperatures were changed from 300°C to 600°C. To examine the microstructural evolution during growth, real-time X-ray scattering was performed at beamline 5C2 at Pohang Light Source (PLS) in Korea. The lattice constant of hexagonal ZnO film can be simply obtained from the reciprocal coordinate (0, 0, 0, $q_\perp$) of the specular ZnO(0002) peak by $a_\perp = 4\pi/q_\perp$, where $a_\perp(q_\perp)$ is the lattice constant (the momentum transfer component) in the substrate normal direction. The lattice strain of ZnO film is defined as $\varepsilon_\perp = [a_\perp - a_\perp(B)]\,/a_\perp(B)$, where $a_\perp(B)$ is bulk lattice constant. The rocking curve measurement was performed for the mosaic distribution of ZnO(0002) planes. In this measurement, we held the X-ray detector at a fixed angle, and rotated

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the sample in various directions. The experimental details are well described in [7].

3 Results and discussions

We first discuss the surface morphology with temperature in the early stage. Figure 1 shows the atomic force microscope (AFM) surface images of the ZnO grown at 300°C [(a) and (b)] and at 400°C [(c) and (d)]. Smooth and layer like surface is observed in the early stage at 300°C, as shown in Fig. 1(a). The surface roughness (root-mean-square, rms) of the film is very small as 1.5 Å, similar to that of the sapphire surface, 1.2 Å. This indicates that ZnO films initially grow as 2D layer mode at the low temperature of 300°C, as previously reported [5]. As the film thickness increases, small dots of 3D islands begin to appear [Fig. 1(b)]. The 3D islands are presumably nucleated on the 2D layers, as generally observed in various lattice mismatched epitaxial films [8]. On the other hand, the 3D islands (small dots) are always observed from the start at high temperatures ($\geq$ 400°C), as typically illustrated in Fig. 1(c) at 400°C. The density of the 3D islands increases with thickness [Fig. 1(d)]. The high resolution transmission electron microscopy image of small ZnO islands shows that there is no 2D-like layer with only bare sapphire surface outside the small islands (data not shown). The surface morphology in Fig. 1 shows that the growth mode of the ZnO/Al_2O_3(0001)

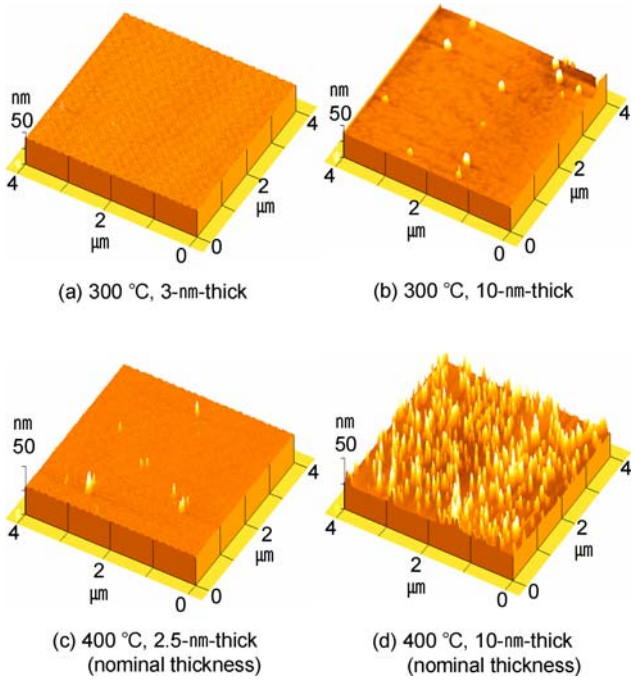

Fig. 1 AFM surface images of ZnO/sapphire(0001) thin films at substrate temperatures of (a) 300°C (3 nm thickness), (b) 300°C (10 nm thickness), (c) 400°C (2.5 nm nominal thickness), and (d) 400°C (10 nm nominal thickness)

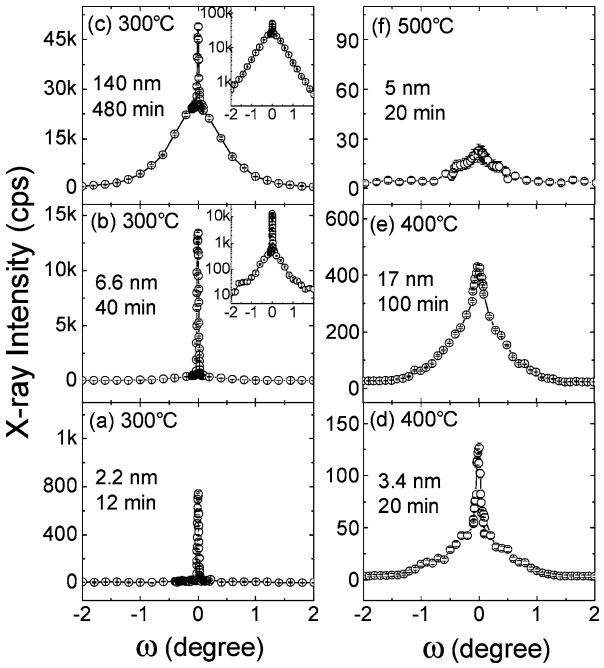

Fig. 2 The rocking curves of ZnO(0002) Bragg reflection at 300°C [(a) 2.2 nm, (b) 6.6 nm, and (c) 140 nm], 400°C [(d) 3.4 nm and (f) 17 nm], and 500°C [(f) 5 nm] as a function of film thickness

seemingly changes from 2D layer to 3D island in early stage with temperature. The growth mode change here, which is different from those in MBE [3] and MOVPE [4], is attributed to the high kinetic energy process of sputter-deposition [9].

To investigate the temperature dependent structural evolution in early stage, we carried out real-time synchrotron X-ray scattering experiments. During deposition, we measured *in situ* the ZnO(0002) reflection profiles for strain calculation and their rocking curves for mosaic distribution. A series of the ZnO(0002) rocking curves with the growth temperature are shown in Fig. 2. At the low temperature of 300°C, only a distinctive very sharp peak is observed in the early stage, as illustrated in Fig. 2(c) for the 2.2 nm thickness films, indicating the 2D layer growth in the early stage at 300°C, consistent with the layer like surface by AFM in Fig. 1(a).

As the film thickness increases, the broad component in the rocking curve, which results from misaligned domains, increases with thickness as shown in Figs. 2(a)–2(c), indicating the continual growth of misaligned domains. Note that the broad component starts to appear in the rocking curve at 6.6 nm thickness, as clearly seen in the inset of Fig. 2(b), plotted in logarithmic scale in the *y*-axis. The misaligned domains are mostly 3D islands grown on the 2D layers [5], as previously observed by AFM in Fig. 1(b). These results show that the 2D layer mode in the early stage changes to 3D with thickness at the low temperature of 300°C.

On the other hand, as the growth temperature increases to 400°C, a narrow component superimposed on a broad

component is observed from early stage as shown in Fig. 2(d) (nominal thickness of 3.4 nm). However, the narrow component, which reflects the existence of aligned domains, is not due to the formation of complete 2D layers as in the ZnO films grown at 300°C. The small dot morphology by AFM in Fig. 1(c) indicated 3D island growth at 400°C. Therefore the existence of the narrow component in the rocking curve and the observation of small dots by AFM suggest that aligned 2D platelets [10] (i.e., 2D islands) nucleate in early stage at 400°C. In addition, the coexistence of the broad component reflects the formation of 3D islands over the 2D platelets. During further growth, the narrow component nearly disappears with concurrent increase in the broad component as shown in Fig. 2(e), indicating the misalignment of the 2D platelets with thickness. At the intermediate temperature of 400°C, 2D platelets nucleate in the very early stage and transform to misaligned state during further growth.

At higher temperatures (≥500°C), however, only broad component is observed in the rocking curve from early stage as shown in Fig. 2(f). The existence of the only broad component and small dots in AFM data clearly suggest that misaligned domains (3D islands) are grown from the start at the high temperatures above 500°C.

From the rocking curves and the AFM data, we conclude that the growth mode of ZnO changes from 2D layer to 3D island in the early stage with growth temperature. At the intermediate temperature of 400°C, however, 2D platelets nucleate in the early stage, act as nucleation cores for the 3D islands and transform to misaligned state during further growth.

Temperature dependence of the strain evolution with thickness in the substrate normal (out-plane) direction is shown in Fig. 3. In the early growth stage, a large lattice strain of up to 0.3% is accumulated in the aligned domains (2D layers) at the low temperature of 300°C whereas the accumulated strain at the high temperature of 500°C is as small as 0.1%. Such a decrease of the lattice strain results

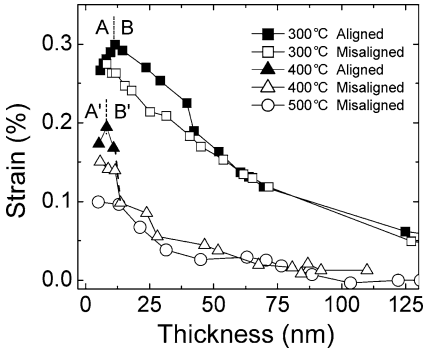

Fig. 3 The temperature dependence of the lattice strain of the ZnO(0002) films as a function of the film thickness in the substrate normal direction

from the growth mode change from 2D to 3D with temperature in the early stage as previously observed by AFM in Fig. 1.

In highly mismatched heteroepitaxial films such as ZnO/sapphire system (18%), the 3D island is a lower-energy configuration than the 2D flat layer because the strain energy can be reduced over its volume with smaller cost of additional surface energy [8]. So the stable configuration of growth mode is 3D islands at high temperatures [11]. At low temperatures, however, 2D layers with high lattice strain are grown at low temperatures [12] because of limited surface diffusion.

At the intermediate temperature of 400°C, the strain of aligned domains is in-between those of 300°C and 500°C in early stage. This is presumably due to the formation of 2D platelets at 400°C. The formation of 2D platelets is attributed to intermediate adatom mobility [10]. By intermediate kinetics, considerable portion of adatoms can be incorporated into edge sites of pre-existing islands as well as on upper layers [13], consequently forming 2D platelets with intermediate strain. The temperature dependence of the lattice strain in the early stage supports that adatom diffusion, which is exponentially dependent on the growth temperature, plays a major role in determining the growth mode of heteroepitaxial ZnO on Al_2O_3(0001).

It is noteworthy that in the initial stages the strain of aligned domains increases with thickness at 300°C and 400°C as shown in the regimes (A) and (A′) in Fig. 3, respectively. Such strain increase in the initial stages is due to the strain accumulation in 2D domains with thickness [14]. The regime of the strain increase gradually reduces with temperature, as illustrated by the regimes (A) at 300°C and (A′) at 400°C, finally disappearing at 500°C. Since the energy barrier to the formation of misfit dislocations is easily overcome at elevated temperatures [15], the strain accumulation is less favorable, consequently diminishing the regime of the strain increase with temperature.

However, the strain of the aligned domains at 300°C begins to decrease at some critical point (indicated by the dashed line) and gradually decreases with thickness, shown in the regime (B). This is due to the introduction of misfit dislocations within 2D layers [15], resulting in an energetically favorable state. A rapid strain decrease observed in the aligned domains at 400°C, shown in the regime (B′), may be due to the existence of many edges at the 2D platelets, since misfit dislocations are dominantly introduced at the edges [8]. As a result, the 2D platelets are rapidly transformed to a misaligned state, consistent with the disappearance of the narrow component in the rocking curve in Fig. 2(e).

In the meanwhile, the strain of the misaligned domains at 300°C gradually decreases from the onset. This is mostly

due to the continual growth of partially relaxed upper layers in the 3D islands [11], as observed in the increase of the broad component in the rocking curves [Figs. 2(b) and 2(c)]. This relaxation mechanism is also applied for the misaligned domains at 400°C and 500°C. At 300°C the strain of the misaligned domains at the onset point is almost as high as that of the aligned ones, presumably because of the homoepitaxial growth of the 3D islands on the 2D layers [5]. The onset of the misaligned 3D domains before the critical point also indicates the continual growth of the 2D layers (up to 12 nm) during the 3D growth.

4 Conclusion

In conclusion, we studied the temperature dependence of growth mode in highly mismatched sputter-grown $ZnO/Al_2O_3(0001)$ heteroepitaxial films using real-time synchrotron X-ray scattering and AFM. The growth mode changes from a highly strained 2D layer to a strain relaxed 3D island in the early stage as the growth temperature increases from 300°C to 500°C. The temperature dependence of the growth mode is attributed to the kinetic energy of adatoms on the surface. By intermediate kinetic energy at 400°C, 2D platelets are nucleated in the early stage, act as nucleation cores of the 3D islands, and shortly transform to a misaligned state by the introduction of misfit dislocations during further growth. The temperature dependence of the lattice strain in the early stage supports that adatom diffusion, which is exponentially dependent on the temperature, plays a major role in determining the growth mode of heteroepitaxial ZnO on $Al_2O_3(0001)$.

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