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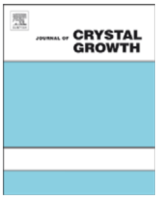

Growth of single-crystalline ZnO film with two-dimensional periodic structure on Si(1 1 1) substrate by molecular beam epitaxy

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ABSTRACT

Single-crystalline ZnO film with two-dimensional periodic structure was grown on Si(1 1 1) substrate by radio-frequency plasma-assisted molecular beam epitaxy. The influence of substrate orientations and growth temperatures was explored for achieving a high-quality ZnO film. It was found that ZnO epilayers grown on Si(1 1 1) substrate have better crystalline quality than the one on Si(1 0 0), and a higher growth temperature was further confirmed favorable for the attainment of a periodic morphology. The results suggest that our growth method is feasible for the fabrication of ZnO film with periodic structure, which is promising for applications in new photonic devices.

As a direct wide band gap (3.37 eV) oxide semiconductor, ZnO has a large exciton binding energy of 60 meV at room temperature, which makes it a potential material in applications of shortwavelength optoelectronic devices [1]. When in a form of photonic crystal structure, ZnO may find more applications in photonic devices, similar to the case of other materials [2–5]. Therefore, many attempts have been made on developing the growth and fabrication techniques to obtain ZnO photonic crystals [6–10], such as electrodeposition method [8] and sol–gel process [10]. However, it is still a challenge to prepare ZnO films with high crystal qualities and good periodic morphologies.

In present work, we have grown ZnO films with two-dimensional periodic structure on Si substrate by radio-frequency plasma-assistant molecular beam epitaxy (rf-MBE) method. The crystalline quality was determined by *in situ* reflection high-energy electron diffraction (RHEED) and *ex situ* X-ray diffraction (XRD). The morphology was characterized by scanning electron microscopy (SEM).

Our ZnO films were grown on Si(1 0 0) and Si(1 1 1) wafers by using a low temperature interface engineering method [11]. The surface of as-received Si substrates had been etched into hole dot arrays by interference lithography gratings, and a two-dimensional periodic structure was hence formed, as shown in Fig. 1. The lattice constant is ~513 nm, and the holes are ~200 nm in depth and ~295 nm in diameter. ZnO film with a similar structure as the substrate was expected to be formed on such surface in epitaxial way, in order to avoid the damage and impurities introduced by nanofabrication process. Element Zn (6N) and Mg (5N) beams were supplied with two commercial Knudsen cells. Active oxygen radicals were produced by a rf-plasma system using high-purity oxygen gas (5N5). Before growth, Si wafers were chemically cleaned in the following procedure: (1) degreased in hot acetone, alcohol and de-ionized water for 5 min with ultrasonic; (2) cleaned in Piranha and rinsed in de-ionized water for 5 min; (3) etched by 5% HF solution for 6 min and rinsed in de-ionized water; (4) dipped in 40% NH_4F for 30 s. Resist coating is removed after steps (1) and (2), and after steps (3) and (4) a hydrogen-passivated Si surface is obtained. After being blown by high-purity nitrogen

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gas, the substrates were loaded into the growth chamber, and then thermally cleaned at 810 °C for 30 min in an ultra high vacuum environment.

During the growth, a three-step low temperature interface engineering technique was adopted [11]. By using this method, a double heterostructure of MgO(1 1 1)/Mg(0 0 0 1)/Si will be formed, which is used to prevent the Si surface from oxidation, and also serves as a template for subsequent ZnO epitaxial growth. In this work, the thickness of the ZnO films was around 500 nm.

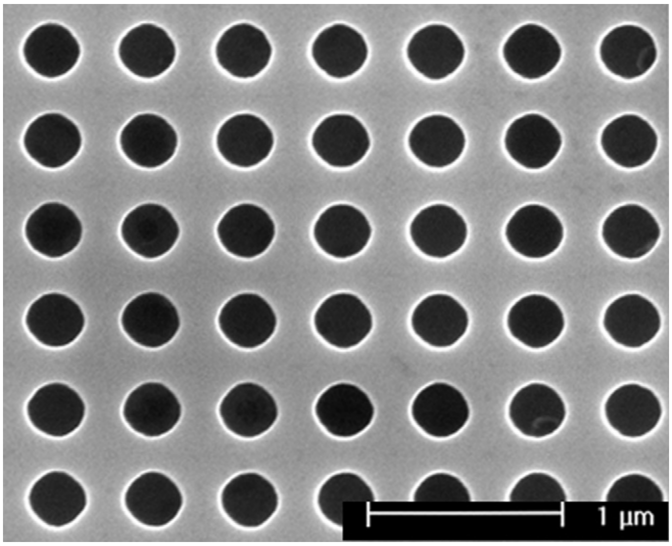

Fig. 1. SEM image of resist coating-free Si dot arrays.

The effect of substrate orientations on the growth of ZnO films was explored. Since Si(1 0 0) wafer dominates in IC industries, we tried the growth on Si(1 0 0) substrate first.

Fig. 2 shows the evolution of RHEED patterns during ZnO growth on Si(1 0 0) substrate, and SEM images of Si(1 0 0) dot arrays and ZnO films. A clear and streaky RHEED pattern of Si(1 0 0) substrate appeared after thermal cleaning at 810 °C (Fig. 2(a)), and a double heterostructure of MgO(1 1 1)/Mg(0 0 0 1)/Si(1 0 0) was formed by using the three-step low temperature interface engineering method, as shown in Fig. 2(b) and (c). The patterns are not well-defined, and multiple domains coexist with the main lattice. The poor crystallinity of MgO(1 1 1)/Mg(0 0 0 1) heterostructure may be attributed to the different surface structures of Si(1 0 0) and Mg(0 0 0 1). The surface structure of Si(1 0 0) is square, but Mg(0 0 0 1) holds a hexagonal structure. They do not match well with each other, hence rotation domains [12] will be caused during epitaxy, which hampered the single-domained ZnO growth (Fig. 2(d)). It indicates that the film grown on Si(1 0 0) at 600 °C has a good *c*-axis preference but with different in-plane orientations.

To study the morphological periodicity of ZnO film, we carried out SEM measurements. In Fig. 2(e), we can clearly see the surface morphology of Si(1 0 0) dot arrays. The holes changed into octagons after chemical etching, because {1 1 0} and other {1 0 0} crystal faces perpendicular to ⟨1 0 0⟩ are dominant and reactive

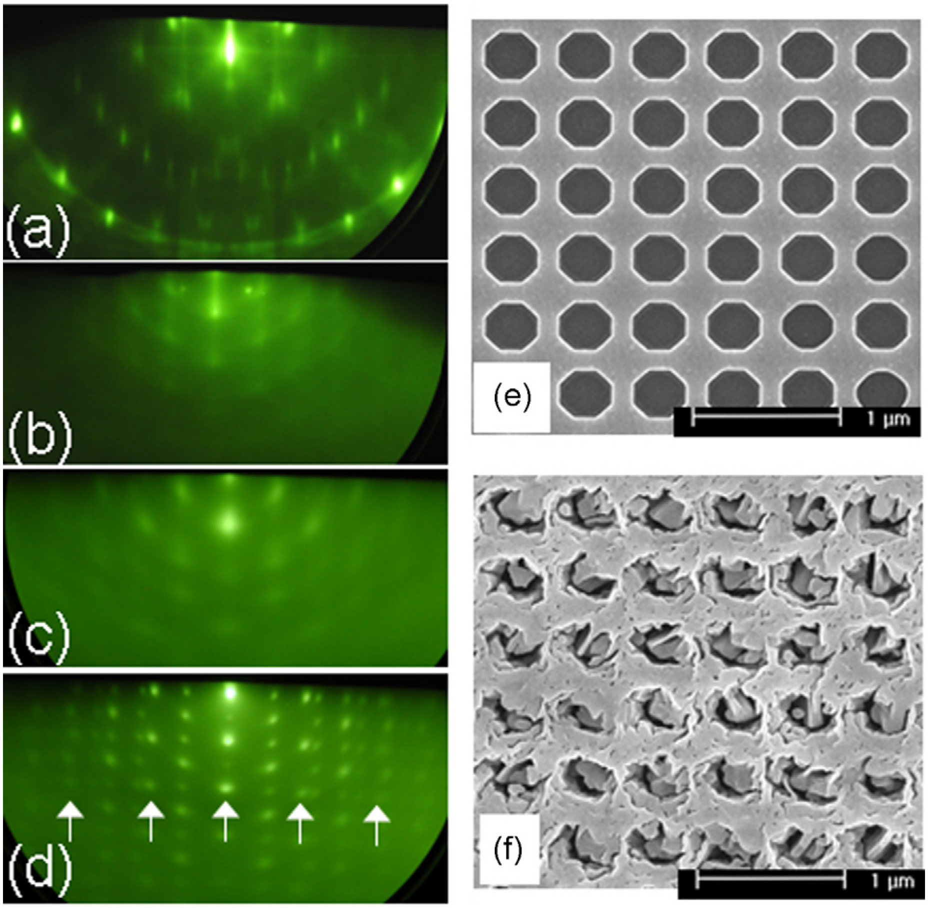

Fig. 2. Evolution of RHEED patterns during ZnO growth on Si(1 0 0) substrate, and SEM images of Si(1 0 0) dot arrays and ZnO film. The electron-beam incidence direction is along Si[1 $\bar{1}$ 0]. RHEED patterns of Si(1 0 0) substrate (a), Mg (b), MgO (c), and ZnO film (d); SEM images of Si(1 0 0) dot arrays (e) and ZnO film (f). The rotation domains in ZnO film are indicated by white arrows in (d).

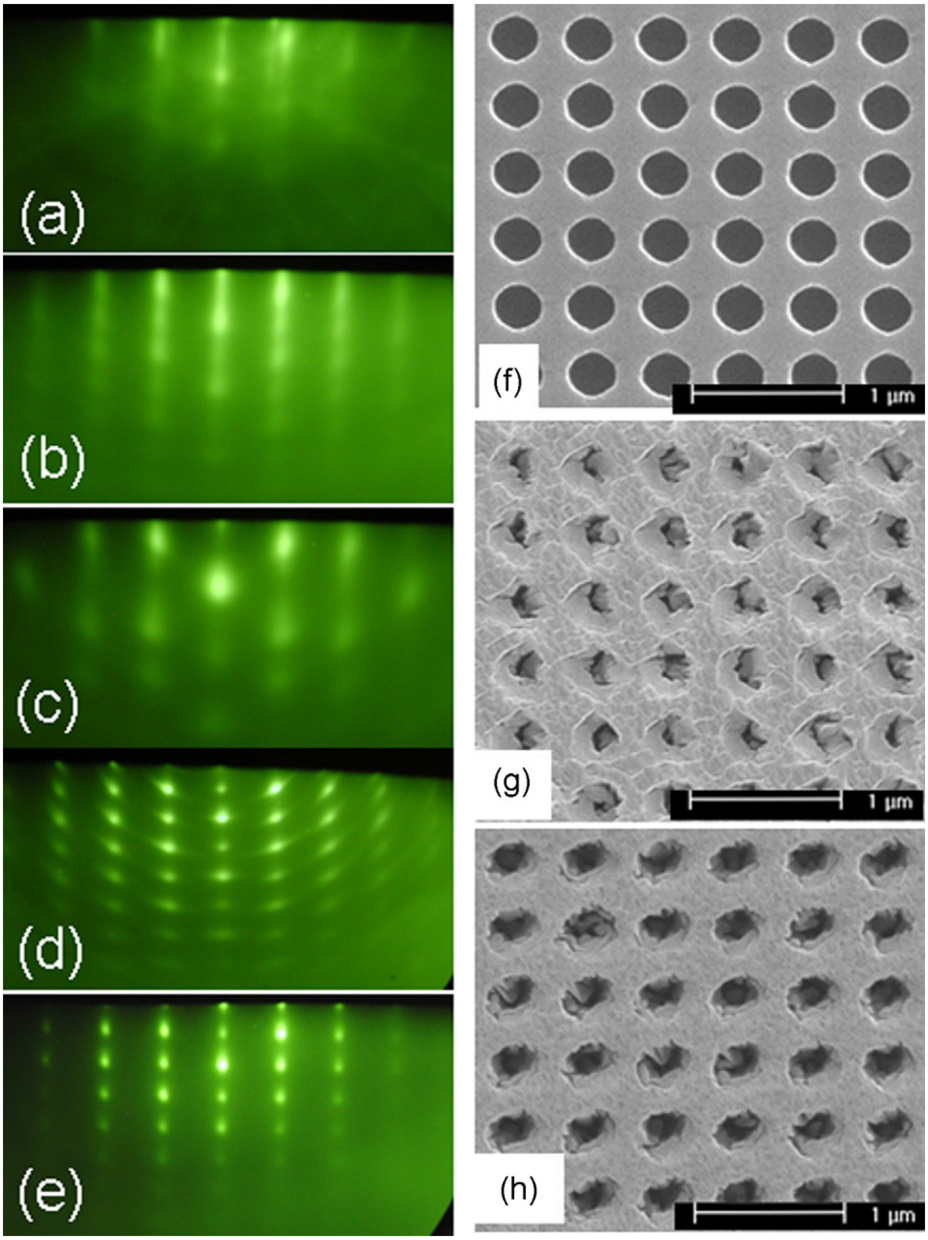

Fig. 3. Evolution of RHEED patterns during ZnO growth on Si(1 1 1) substrate, and SEM images of Si(1 1 1) dot arrays and ZnO films. The electron-beam incidence direction is along Si[1 0 $\bar{1}$]. RHEED patterns of Si(1 1 1) substrate (a), Mg (b), MgO (c), ZnO film grown at 450 °C (d), and ZnO film grown at 600 °C (e); SEM images of Si(1 1 1) dot arrays (f), ZnO film grown at 450 °C (g), and ZnO film grown at 600 °C (h).

crystal faces, which will keep their shapes when etched by HF solution. It is supposed that the octagonal holes may be one of the reasons that gave rise to the poor periodic morphology (Fig. 2(f)) and crystal quality of ZnO film. To improve that, some new interface engineering technologies should be developed.

The crystalline quality of ZnO film will be degraded to a great extent due to the existence of rotation domains, which hampers the potential applications of such material. Therefore, we altered to Si(1 1 1) substrate, where the same three-step low temperature interface engineering technology was also applied.

Thermally cleaned Si(1 1 1) substrate at 810 °C shows a clear and streaky RHEED pattern (Fig. 3(a)). Different from the case of Si(1 0 0), however, the RHEED patterns of Mg(0 0 0 1) and MgO(1 1 1) thin layers on Si(1 1 1) demonstrate clear hcp and rocksalt structures, respectively (Fig. 3(b) and (c)). The rotation domains were absent, and single-crystalline ZnO films were readily achieved on Si(1 1 1) substrate, as shown in Fig. 3(d) and (e). These results indicate the strong dependence of single-crystalline ZnO film growth on Si(1 1 1) wafer. It should be noted that the ZnO films were grown at 450 and 600 °C, respectively. At a lower growth temperature (450 °C), the ZnO epilayer showed an inferior crystal quality. The loop-like diffraction spots indicate that it had a polycrystal tendency (Fig. 3(d)). On the other hand, the ZnO epilayer deposited at a higher temperature (600 °C) demonstrates a better crystal quality, as shown in Fig. 3(e). The sharp spots imply that it is a single-crystalline film with good quality.

The periodicity of a photonic crystal plays a key role in determining its optical properties. The effect of growth temperature on the periodic morphology of ZnO films was hence investigated for the films grown at 450 and 600 °C on Si(1 1 1) substrate. Fig. 3(f)–(h) show the SEM images of Si(1 1 1) dot arrays and ZnO films. In Fig. 3(f), the holes of chemically etched Si(1 1 1) dot arrays still keep their original shapes (Fig. 1), because there are no dominant crystal faces perpendicular to Si(1 1 1) surface.

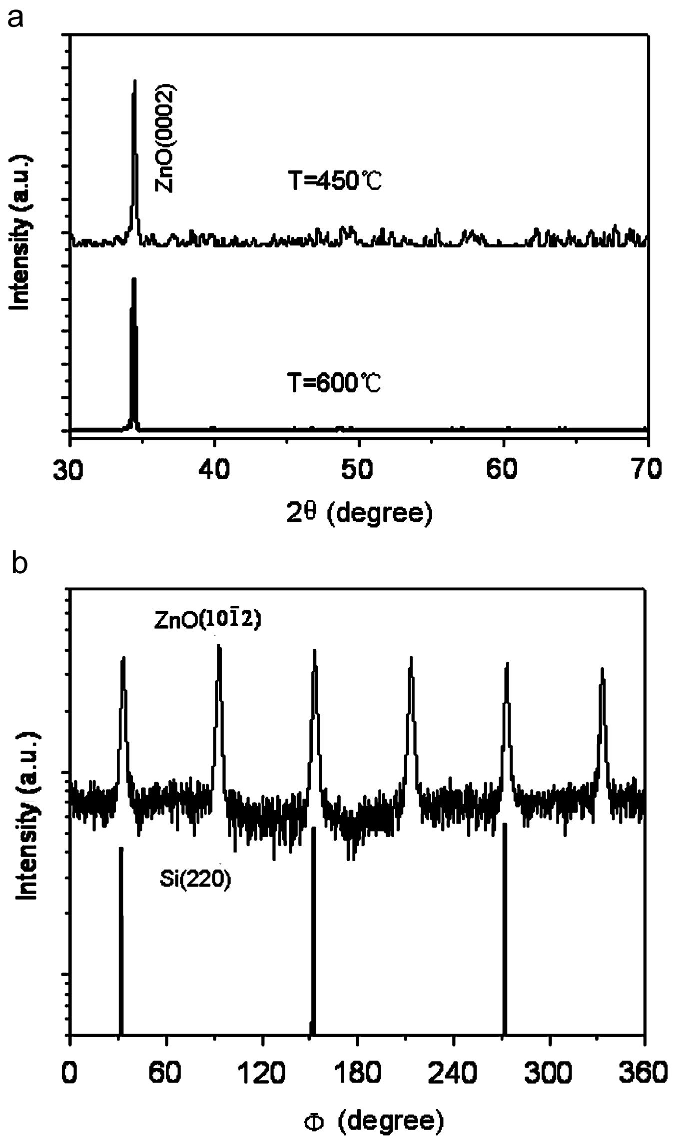

Fig. 4. XRD spectra of ZnO films grown on Si(1 1 1) substrate: (a) θ–2θ scan; (b) Φ scan of ZnO (1 0 $\bar{1}$ 2) and Si(2 $\bar{2}$ 0) planes.

Fig. 3(g) and (h) are the SEM images of ZnO films grown at 450 and 600 °C. In the case of a lower growth temperature, the surface mobilities of atoms are not high enough, and it is difficult for them to find the right positions and achieve a good periodic morphology (Fig. 3(d)). After increasing the growth temperature, however, the diffusion abilities of atoms are enhanced, and the morphological periodicity was hence improved (Fig. 3(h)).

To testify the effect of higher growth temperature on improving the crystal quality of ZnO film grown on Si(1 1 1) substrate, XRD measurements were performed. Fig. 4(a) shows the θ–2θ scan results, and only ZnO(0 0 0 2) diffraction peaks can be found. It suggests that both of the ZnO films are grown strictly along *c*-axis. Furthermore, the ZnO film grown at 600 °C has a narrower full-width at half-maximum value (0.15°) than the film grown at 450 °C (0.19°), which indicates the role of higher growth temperature in improving the crystalline quality. To further study the symmetry of ZnO film grown at 600 °C, Φ scan tests were carried out on ZnO(1 0 $\bar{1}$ 2) and Si(2 2 0) planes (Fig. 4(b)). In 360° scan range, only one set of six diffraction peaks can be detected in the film, which means that the film has a single-domain wurtzite structure. This result is consistent with the corresponding RHEED observations.

In summary, a single-crystalline ZnO film with good two-dimensional periodic morphology was obtained on Si(1 1 1) at 600 °C by using rf-MBE. It is found that the substrate orientation and growth temperature have direct influence on the accomplishment of a ZnO film with good qualities. The results suggest that our method is feasible for fabricating ZnO film with two-dimensional periodic structure, which is promising for applications in new photonic devices.

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