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Growth of Single Crystalline ZnO Films on 18%-Lattice Mismatched Sapphire Substrates via Inverse Stranski-Krastanov Mode

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Abstract

We report a new growth mode of heteroepitaxy, inverse Stranski-Krastanov (SK) mode, in which three dimensional (3D) islands initially form and two-dimensional (2D) layer subsequently grows on the 3D islands. This 3D-2D transition, just opposite to 2D-3D transition in the well-known SK mode, is triggered by sudden change in the surface energy through impurity adsorption/desorption behavior. By using this mode, single crystalline ZnO films have been grown on 18%-lattice mismatched sapphire substrates, where nitrogen has been employed as an impurity. The resultant films possess atomically-flat surface and high crystal quality, where the full width at half maximum of (002) x-ray rocking curves are 36 arcsec. We believe that our findings on this growth mode will offer a new approach for single crystal growth "beyond" lattice matching condition.

1. Introduction

Success in semiconductor devices has been limited thus far because of lattice-mismatch problems between growth layers and substrate. Regarding heteroepitaxy on large lattice mismatched substrates, there are two primary modes by which thin films grow: 1) Volmer–Weber (VW: island formation) mode and 2) Stranski–Krastanov (SK: layer-plus-island) mode. In both modes, crystal growth ends up in formation of three-dimensional (3D) island, making fabrication of single crystalline films on lattice-mismatched substrates challenging.

In this context, we propose another growth mode, "inverse" SK mode (island-plus-layer growth mode), which enables us to grow single crystalline films even on large lattice mismatched substrates (Fig. 1(b)). In a conventional SK mode (Fig. 1(a)), a highly strained two-dimensional (2D) layer initially form, taking the advantage of the low surface energy. As 2D layer grows, however, the total free energy increases because the elastic energy stored in the system increases. Finally, at a critical thickness, 2D to 3D growth mode transition occurs so that the lattice strain is relaxed. In the inverse SK mode, in contrast, we initially grow nanosized 3D islands by using "impurity" that lower the surface energy. Since the elastic strain due to lattice mismatch is relaxed through the island formation, such 3D islands have low density of misfit dislocation, resulting in good in-plane and out-of-plane alignment of the crystal axis. After lattice strain is relaxed, we desorb the impurity atoms from the surface to increase the surface energy, and thus lead to coalescence of 3D islands (2D layer formation).

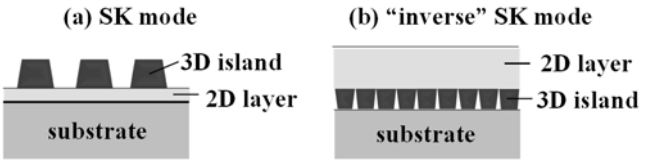

Fig. 1. Schematic of growth modes of heteroepitaxy for large lattice mismatched systems: (a) SK mode and (b) "inverse" SK mode.

Here, we demonstrate inverse SK growth of single crystalline ZnO films on 18%-lattice mismatched sapphire substrates, where nitrogen is employed as impurity. The roles of impurity that leads to inverse SK growth are also discussed.

2. Experimental

All films were fabricated by radio-frequency magnetron sputtering using ZnO ceramic targets. First, 3D island layers of 10 nm thickness were deposited on sapphire substrates in N_2/Ar atmosphere. Next, 2D layers were deposited on the 3D island layers in O_2/Ar atmosphere. The total thickness was 10–1000 nm.

3. Results and discussion

We have successfully grown ZnO single crystals on sapphire substrates via inverse SK mode. AFM images in Fig. 2 show the evolution of surface morphology upon deposition of (a) 10 nm, (b) 12 nm, (c) 15 nm, (d) 20 nm, (e) 30 nm, (f) 200 nm, (g) 1000 nm of ZnO films. Here, we first deposited 10-nm-thick ZnO films with N_2 gas, then cease supplying N_2, and deposited ZnO films without N_2. For comparison, an AFM image of a 1000-nm-thick ZnO film fabricated without N_2 through all stages is shown in Fig. 2(h). In the case with N_2, nanosized 3D islands initially grow (Fig. 2(a)), and they rapidly coalesce to form 2D layer after cessation of N_2 supply (Figure 2(b)–(e)). Eventually, ZnO films grow in 2D mode, where the films have atomically-flat surface with steps of 0.26 nm-height, corresponding to the half of c-axis length of ZnO (Fig. 2(f) and (g)). This crystal growth via 3D-2D mode transition, just opposite to 2D-3D transition in the well-known SK mode, is what we call inverse SK mode. In the case without N_2, by contrast, ZnO film grows in a 3D mode through all growth stages. The resultant 1000-nm-thick

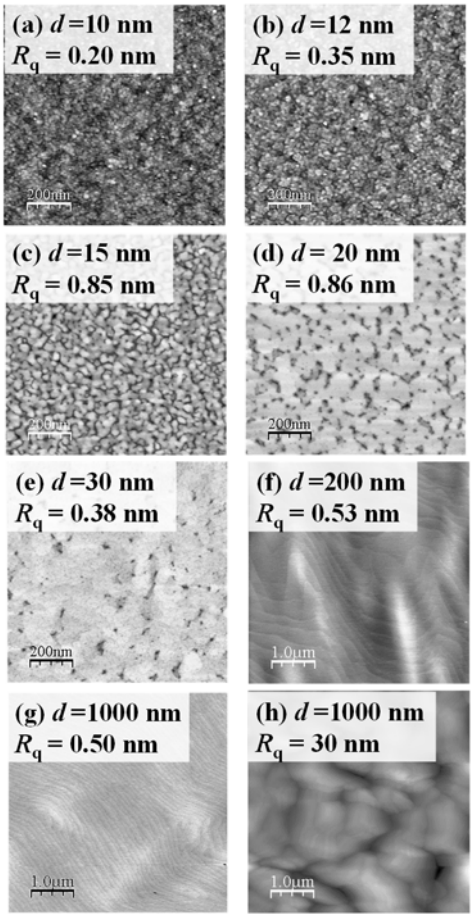

Fig. 2. AFM images showing the evolution of surface morphology upon deposition of (a) 10 nm, (b) 12 nm, (c) 15 nm, (d) 20 nm, (e) 30 nm, (f) 200 nm, (g) 1000 nm of ZnO films. Here, we first deposited 10-nm-thick ZnO films with N_2, then cease supplying N_2 gas, and deposited ZnO films without N_2. For comparison, an AFM image of a 1000-nm-thick ZnO film fabricated without N_2 through all stages is shown in Fig. 2 (h)

film has 3D columnar structures as shown in Fig. 2(h), and the root-mean-square (RMS) roughness (R_q) of the surface is significantly large of 30 nm. These results clearly show that N_2 plays a key role in determining the growth mode of ZnO films on sapphire substrates.

High crystal quality of ZnO films grown in inverse SK mode (fabricated with N_2) was proved by x-ray diffraction analysis. The full width at half maximum (FWHM) of (002) and (101) rocking curves are 36 and 335 arcsec, respectively, significantly small compared with those of ZnO films grow without N_2 (900 and 1260 arcsec, respectively). ZnO films grown in inverse SK mode possess high crystal quality with good in-plane and out-of-plane alignment of the crystal axis.

Now we discuss the role of nitrogen during inverse SK growth. Figure 4 shows AFM images of 10-nm-thick ZnO films fabricated with and without N_2. Significant changes in the grain size and in the surface roughness are observed. The grain size of the film deposited with N_2 is about 10 nm, which is one order of magnitude smaller than that deposited without

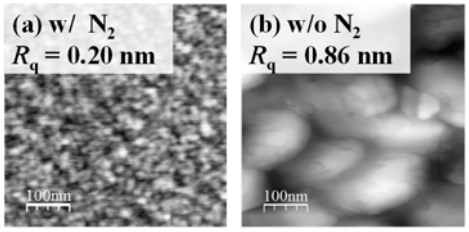

Fig. 3. AFM images of 10-nm-thick ZnO films fabricated with N_2 (a), without N_2 (a).

N_2. Since N_2 themselves are chemically stable, we consider that nitrogen atoms, produced through N_2 dissociation, play important roles in determining the island size. In fact, we observed nitrogen atoms of 10^{10} cm^{-3} in the plasma by vacuum ultraviolet absorption spectroscopy [1]. This value is comparable to the oxygen atom density originating from ZnO sputtering targets. In contrast, the concentration of nitrogen atoms in ZnO film is significantly small of $10^{17–18}$ cm^{-3}, which is 4–5 orders of magnitude lower than the oxygen concentration in the film. These results indicate the low solubility of nitrogen in ZnO, and this nature is what we consider to lead to grain size decrease. That is, the low solubility make nitrogen atoms segregate to the surface as well as to the grain boundaries, and thus lower the surface free energy per unit area [2]. As a result, relaxed small islands form because the gain of elastic relaxation energy overcompensates the cost due to extra surface energy (a smaller island has a higher surface-to-volume ratio). After cessation of N_2 supply, the surface energy drastically increase. This sudden increase in the surface energy provides a strong driving force for coalescence of 3D islands, and consequently causes 3D to 2D mode transition as described above.

4. Conclusions

We demonstrate inverse SK growth of single crystalline ZnO films on 18%-lattice mismatched substrates. In the inverse SK mode, nanosized 3D islands initially grow, and then 2D layer subsequently grow on the 3D islands. We found that nitrogen impurity, which leads to drastic change in the surface energy, plays a key role in the inverse SK mode. In spite of the large lattice mismatch, the resultant ZnO films possess high crystal quality along with atomically-flat surface. We believe that our findings will offer a new method of single crystal growth “beyond” lattice matching condition.

Acknowledgements

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