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A Novel Buffer Layer using Titanium-Oxide for ZnO epitaxial growth on Sapphire

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1. Introduction

ZnO has been expected to apply to blue- or ultraviolet light-emitting devices because of their properties with a wide direct band gap of 3.37eV. However, it has been recognized that undoped ZnO indicates high n-type conductivity due to oxygen deficiency and/or interstitial-Zn, which are probably introduced during the growth at high temperatures and by poor reactivity of the supplied oxygen. Plasma-assisted epitaxy (PAE) is a possible process to reduce the defects by reactive oxygen supply. Additionally, low temperature growth can be achieved by PAE using the momentum of excited species in plasma. Recently, we demonstrated that ZnO can be epitaxially grown on C-sapphire substrate using oxygen-gas plasma by PAE at low temperature as low as 400°C with suppressing the defects [1,2] and nitrogen can be doped as shallow acceptors with activation energy about 150meV [3]. However, in the case of high nitrogen-doping, the surface roughness was increased and the optoelectronic property was remarkably degraded by strong self-compensation incorporated compensation donors. Thus, it should be concluded that non-thermal equilibrium growth at lower temperatures than 400°C with smooth surface is required to achieve p-type ZnO growth.

The purpose of this paper is to propose a novel buffer layer using Titanium-oxide to reduce residual donor in ZnO and achieve epitaxial growth at lower temperatures with smooth surface.

2. Experimental

ZnO was grown at low temperature about 340°C by PAE. High-purity elemental Zn (6N) and oxygen gas (6N) were used as sources. The oxygen gas was excited by radio-frequency power (rf-power) at 13.56MHz through a capacitive coupling. High purity elemental Zn was evaporated from Knudsen cell through a nozzle with a small hole and supplied to the growth surface through the oxygen plasma with the excited oxygen species. Detailed PAE apparatus is described elsewhere [3]. (11-20)Al₂O₃ (A-sapphire) and (0001) Al₂O₃ (C-sapphire) with mirror surface were used as substrates. The substrates were cleaned by organic-solvents and H₂SO₄+H₂O₂ and then

etched by a hot H₂SO₄+H₃PO₄ solution for 15minutes.

Titanium oxide buffer layer was grown at low temperatures ranging from 290°C to 340°C in 3mtorr on the A-sapphire by low-pressure chemical vapor deposition (LPCVD) using Titanium tetra-iso-propoxide (TTIP) and oxygen gas (6N) as sources. The TTIP was vaporized in a hot quartz-bath at 70°C and introduced into the chamber through a hot alumina nozzle at 85°C.

Optoelectronic property of ZnO films was examined by photoluminescence (PL) at 10K. Xe-Hg deep UV-lamp was used as excitation light source, where the light around 313nm was selected by a band-pass filter and then irradiated to the ZnO layers through a sapphire window.

3. Results and discussions

Previously, we found out Ti₂O₃ layer with corundum structure are epitaxially grown on A-sapphire by the LPCVD [4]. Figure 1 shows XRD pattern of 500nm-thick titanium oxide layer grown on A-sapphire, where (0001)Ti₂O₃ layer is epitaxially grown. It is expected that lattice mismatching is relaxed using such thick-Ti₂O₃ layer as buffer layer in contrast to the heteroepitaxial system of ZnO/C-sapphire, because the lattice mismatch between C-plane ZnO and C-plane Ti₂O₃ in plane, which is 9.2%, is smaller than the value between C-sapphire and C-plane ZnO in plane, which is 18%. In the system of ZnO/thick-Ti₂O₃, the grain size of ZnO was grater than that on C-sapphire and very strong and sharp donor-bound exciton (D⁰X) emission was observed on PL property.

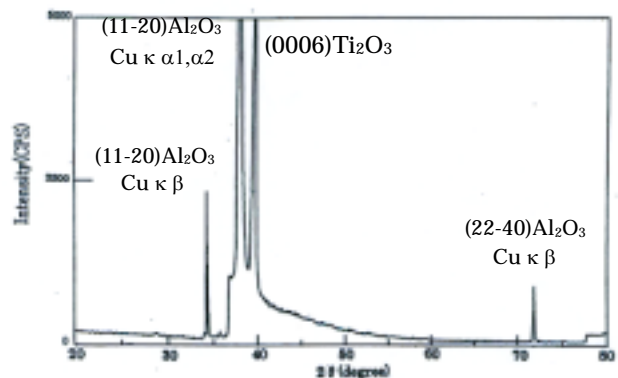


Figure 1 XRD pattern of titanium oxide layer grown on A-sapphire.

However, the grains were three-dimensionally grown and residual donor that is probably interstitial-Zn could not be reduced. On the other hand, the surface morphology and the PL property were drastically improved by the thin-Ti₂O₃ buffer layer.

Figure 2 shows PL spectra of ZnO film grown on (a) C-sapphire at 400°C and (b) the thin buffer layer on A-sapphire at 340°C, where the ZnO layer on the buffer layer was epitaxially grown with C-plane surface. Nevertheless, ZnO layer was grown at lower temperature, free-exciton emission peaked at 3.377eV(A-Ex) and 3.386eV(B-Ex) were clearly observed with a sharp D⁰X emission from the layer on the buffer layer, in contrast to the weak emission from the layer grown on C-sapphire. The property was remarkably dependent on the growth condition and the thickness of buffer layer.

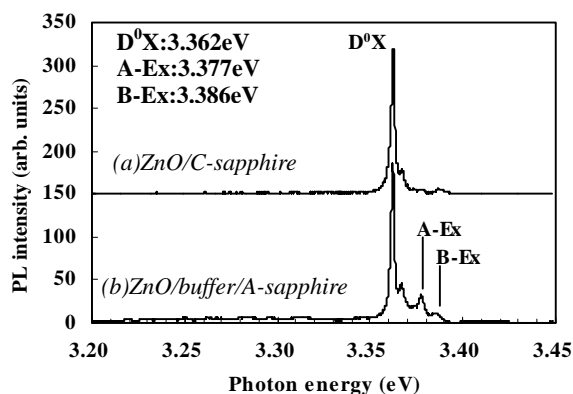


Figure 2 PL spectra of ZnO (a) on C-sapphire and (b) on A-sapphire with thin buffer layer.

Figure 3 shows dependence of exciton emission intensities on buffer layer thickness, where the buffer layer was grown at 300°C. Free-exciton emission was increased with increasing the buffer thickness and decreased above 0.8nm thickness of the layer. Optimum buffer thickness can be estimated around 0.8nm from the result. It should be noted here the D⁰X emission was drastically decreased in the ZnO layer on the optimized buffer layer. These results indicate that the residual donor in ZnO can be reduced by the very thin buffer layer about 0.8nm-thickness. Additionally, the ZnO layer with mirror surface can be obtained on the optimized buffer layer.

Figure 4 shows PL spectrum of ZnO film grown on the optimized titanium-oxide buffer layer, where the growth condition of ZnO layer at 340°C was also optimized. The spectrum was dominated by strong free-exciton emission (A-Ex) and indicates that the residual-donor was well suppressed in the layer. The inset of Fig. 4 shows surface

morphology by Nomarski microscope of ZnO layer. A few hexagonal pyramids with same facet due to tree-dimensional growth were observed but most of the surface was mirror-like which was achieved by two-dimensional growth.

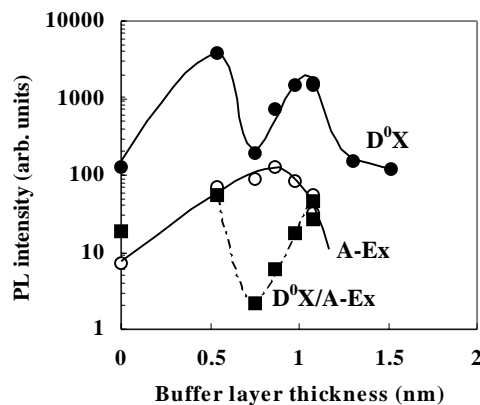


Figure 3 PL intensities of ZnO films on buffer layer as a function of buffer layer thickness.

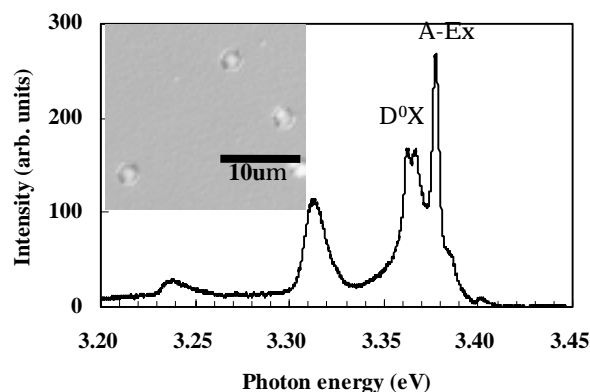


Figure 4 PL spectrum of ZnO film on the suitable buffer layer

4. Conclusions

Ti₂O₃ buffer layer was demonstrated for ZnO growth. The very thin buffer layer about 0.8nm-thickness is so effective to prevent residual donor and enhance the two-dimensional growth. It is considered that the residual donor is easily introduced in the layer by three-dimensional growth. It is believed that the present buffer layer introduces to the fabrication of p-type ZnO growth.

References

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