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Effect of hydrogen irradiation during growth on molecular beam epitaxy of ZnO

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1. Introduction

Control of the conductivity and band gap engineering are necessary for realization of ZnO-based optical devices. Recently, despite successful growth of N-doped *p*-ZnO [1-3], the reproducibility of *p*-ZnO films seems to be yet problematic. The problem is due in part to the residual electron concentration whose origin has not yet been determined, but possible origins include intrinsic point defects or residual impurities. Another remaining problem in achieving successful growth of *p*-ZnO films is the low solubility and low incorporation rate of N species in ZnO. Such incorporation decreases with increasing growth temperature [4]. A low temperature is also advantageous for the growth of homogeneous ZnO-based alloys such as ZnCdO and ZnMgO, because a high temperature enhances compositional fluctuations [5,6]. Therefore, a low-temperature technique to grow ZnO with good crystal quality needs to be developed. To grow high-quality films at low temperature, the reduction of surface diffusion of adatoms should be prevented. Termination of the surface with hydrogen atoms is an effective technique for such a reduction. The purpose of this study is to confirm the effect of hydrogen in molecular beam epitaxy (MBE) growth of ZnO films. Our results reveal that (a) H_2 irradiation during growth enhances the surface migration of adatoms, significantly improving both the surface morphology and crystal quality of ZnO films at low-growth temperature of 300°C; (b) hydrogen apparently does not act as a dominant donor species in undoped ZnO grown even under H_2 irradiation.

2. Experimental procedure

ZnO films were grown on *a*-plane sapphire [(11-20) α-Al_2O_3] at low temperature (300°C) using MBE with molecular hydrogen irradiation at various H_2 flow rates and without such irradiation. A radio-frequency (rf) oxygen plasma was used as the oxygen source, and elemental Zn evaporated from a Knudsen cell was used as the Zn source. Atomic hydrogen used for cleaning of a substrate was generated by using a tungsten filament heated at 1800°C. A sapphire substrate was degreased by ultrasonic cleaning in acetone and methanol followed by chemically etching in H_2SO_4:H_3PO_4 = 3:1 at 110°C for 30min. Prior to growth, the substrate was exposed to atomic hydrogen (2.0 sccm) at 800°C for 30 min. A ZnO buffer layer was grown at 450°C to a thickness of ca. 40 nm and then, to improve surface smoothness, annealed at 900°C for 5 min. A ZnO film was grown on this buffer layer at substrate temperature as low as 300°C under molecular hydrogen (without cracking) irradiation with various H_2 flow rates (FR_{H2}) of 0 to 2.0 sccm at slightly Zn-rich growth condition. The Zn beam flux of 0.15 nm/s, oxygen flow rate of 1.0 sccm, and rf power of 190 W were used in these growth. The total film thickness was 0.9 μm. Atomic force microscopy (AFM), x-ray diffraction (XRD), Hall effect measurements and secondary ion mass spectrometry (SIMS) were used to characterize these ZnO films.

3. Results and Discussion

The grain size of ZnO film was estimated from surface observation of AFM. Figure 1 shows the grain size of ZnO films grown with and without H_2 irradiation as a function of growth temperature. Assuming that the diffusion length of adatoms is reflected by the grain size, the diffusion lengths in H_2-assisted MBE are enhanced 7-fold for FR_{H2} = 1 sccm and 10-fold for 2 sccm, respectively, in comparison with no H_2-assisted MBE. The surface diffusion length in H_2-assisted MBE of ZnO at 300°C approached that of MBE of ZnO at 600°C without H_2 irradiation.

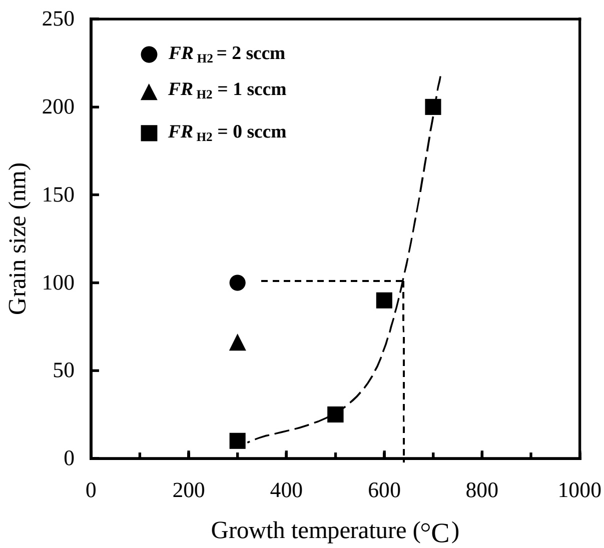

Fig. 1 Correlation between grain size and growth temperature.

The crystalline quality of the ZnO films was evaluated by measuring symmetric (002) and skew symmetric (100) x-ray ω-rocking curves (XRCs). Figure 2 shows the full width at half maximum (FWHM) values of (002) and (100) XRCs for ZnO films as a function of growth temperature. With increasing grain size as shown in Fig. 1, the mosaicity of the crystal lattice decreased, yielding improved crystal quality. The FWHM values of (002) and (100) XRCs for a ZnO film grown at 300°C without H_2 irradiation were 807 and 1774 arcsec, respectively, indicating poor crystalline quality. On the other hand, the FWHM values of (002) and (100) XRCs for a ZnO film grown with FR_{H2} = 2 sccm narrowed to 425 and 880 arcsec, respectively. These FWHM values are in the range of the typical FWHM values of a ZnO film grown at 500°C without H_2 irradiation.

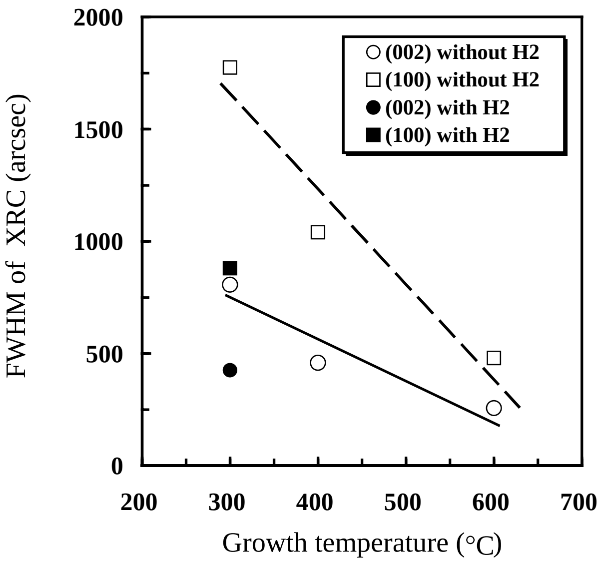

Fig. 2 Correlation between between the FWHM of (002) and (100) ω-scan X-ray rocking curves and growth temperature.

The electrical properties such as mobility and carrier concentration of the ZnO films were evaluated by Hall effect measurement using van der Pauw method. When the growth temperature for ZnO films without H_2 irradiation was decreased from 600 to 300°C, the carrier concentration increased from 1.30×10^{17} to 2.26×10^{17} cm^{-3} and the electron mobility decreased from 111 to 44 cm^2/(Vs). Interestingly, the electron carrier concentration decreased from 2.26×10^{17} to 1.80×10^{17} cm^{-3} and electron mobility increased from 44 to 110 cm^2/(Vs) with H_2 irradiation. The electrical properties of ZnO films grown at 300°C were improved by performing H_2 irradiation. We confirmed from SIMS measurement that the residual impurities in ZnO film did not account for the improvement in electrical properties by H_2 irradiation. The H_2 irradiation improved the crystalline quality of the ZnO film. The XRD results (Fig. 2) show that the tilt and twist of ZnO films were significantly reduced by the H_2 irradiation during growth, suggesting a reduction in the number of dislocations. In GaN films, the dominant electron scattering mechanism in the low electron concentration region is dislocation scattering [7]. We recently reported that a decrease in dislocation density improved the electrical properties of ZnO [8]. The estimated dislocation density in the ZnO films grown here with FR_{H2} = 2 sccm was 1.5×10^9 cm^{-2}, whereas that in ZnO without H_2 irradiation was 6.0×10^9 cm^{-2}. Therefore, the observed changes in electrical properties of the ZnO films are likely caused by a reduction of dislocation density.

4. Conclusions

The effect of hydrogen on growth and crystalline quality of ZnO films grown at low temperature (300°C) by MBE was investigated. With increasing irradiated H_2 flow rate during growth from 0 to 2 sccm, the grain size in ZnO increased from 10 to 100 nm due to enhancement of the surface diffusion of adatoms. The structural and electrical properties of the ZnO films grown at 300°C were significantly improved by the irradiation of molecular hydrogen: the FWHM values of the the (002) and (100)XRCs were from 807 to 425 arcsec and from 1774 to 880 arcsec, respectively; the electron concentration degreased from 2.26 $\times 10^{17}$ to 1.80×10^{17} cm^{-3}; and the electron mobility increased from 44 to 110 cm^2/(Vs). The ZnO grown with H_2 irradiation had a crystalline quality as high as ZnO grown at 600°C without H_2 irradiation.

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