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Single crystalline ZnO films grown on lattice-matched ScAlMgO$_4$(0001) substrates

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Lattice-matched ($\Delta a/a = 0.09\%$) ScAlMgO$_4$(0001) substrates were employed to grow single crystalline quality ZnO films by laser molecular-beam epitaxy. Extremely smooth surface represented by atomically flat terraces and half unit cell (0.26 nm) high steps and extremely small orientation fluctuations both in-plane ($<0.02°$) and out-of-plane ($<0.01°$) are achieved. The films have high mobility (~ 100 cm^2/V s) together with low residual carrier concentration ($\sim 10^{15}$ cm^{-3}). Excellent optical properties, including a clear doublet of A and B exciton peaks in absorption spectra, were also observed. These features could not be simultaneously achieved for ZnO films grown on sapphire(0001) having a large lattice mismatch ($\Delta a/a = 18\%$). © *1999 American Institute of Physics.* [S0003-6951(99)05743-5]

As an oxide wide band gap ($E_g = 3.37$ eV) semiconductor, ZnO has attracted considerable attention for applications such as ultraviolet light emitting devices and laser diodes, due to the observation of very efficient ultraviolet excitonic laser action starting at very low threshold of optical pumping even at room temperature.[1] Mg$_x$Zn$_{1-x}$O alloy films were readily prepared to extend the band gap up to about 4.0 eV.[2] ZnO/Mg$_x$Zn$_{1-x}$O superlattices[3] were demonstrated to confirm the quantum size effect.[4] However, synthesis of *p*-type ZnO still remains the most critical issue and a big challenge. The history of ZnSe and GaN tells us that high quality intrinsic films having high carrier mobility and low residual carrier concentration are the starting point. ZnO thin films grown on lattice mismatched ($\sim 18\%$) sapphire(0001) substrates are epitaxial but stay multicrystalline in nature having incoherent grain boundaries. Actually, these grain boundaries in epitaxial ZnO thin films seem to be useful for observing excitonic laser action. When the nanocrystal size is tuned to as small as 50 nm, excitonic lasing is most efficient, making use of these grain boundaries as mirrors of longitudinal cavity. The electronic properties of such films are rather poor as represented by typical electron concentration, $n \sim 10^{17}$ cm^{-3} and Hall mobility $\mu \sim 10$ cm^2/V s at room temperature, compared to $n \sim 10^{15}$ cm^{-3} and $\mu \sim 200$ cm^2/V s for bulk single crystals.[5]

One may overcome these problems by using lattice-matched substrates. We have selected hexagonal ScAlMgO$_4$(0001) with lattice constants of $a = 3.246$ Å and $c = 25.195$ Å (Ref. 6) having an in-plane lattice mismatch as small as 0.09%. ScAlMgO$_4$ is considered to be a natural superlattice composed of alternating stacking layers of wurtzite(0001)-face (Mg, Al)O$_x$ and rocksalt(111)-face ScO$_y$ layers, and hence has a cleavage habit along the (0001) plane. High quality single crystals can be grown by the Czochralski method.[7] Its crystal structure and a possible hetero-interface with ZnO are schematically shown in Fig. 1.
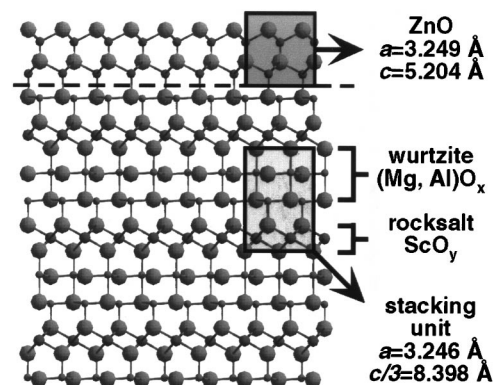
Here, we report the growth of single crystalline ZnO

FIG. 1. Schematic illustration of ScAlMgO$_4$ crystal structure composed of an alternating stack of wurtzite (Mg, Al)O$_x$(0001) and rocksalt ScO$_y$(111) layers. Epitaxially grown ZnO is attached by assuming that the wurtzite layer of ScAlMgO$_4$ coherently continues with that of ZnO.

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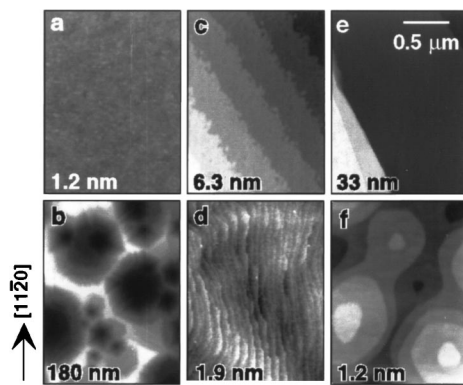[c]Electronic mail: kawasaki@oxide.rlem.titech.ac.jp

FIG. 2. Atomic force microscope images of various substrates and the films deposited on them. (a) and (b) As-polished sapphire(0001). (c) and (d) As-polished ScAlMgO$_4$(0001). (e) and (f) cleaved ScAlMgO$_4$(0001). Films were 1.5 μm thick grown at 1000 °C. The step height in (c) is 0.85 nm, and that in both (d) and (f) is 0.26 nm, corresponding to charge neutral units of ScAlMgO$_4$ and ZnO, respectively. The span of gray scale in the topographic image is given in the respective left-bottom corner.

films on lattice-matched ScAlMgO$_4$(0001) substrates and demonstrate excellent structural, electric and optical properties which would serve as host crystal films for possible *p*-type doping.

ZnO thin films were grown on ScAlMgO$_4$(0001) and sapphire(0001) substrates by laser molecular-beam epitaxy that has been widely applied to the growth of high quality oxide thin films under high vacuum conditions.[8] KrF excimer laser pulses were directed onto a ZnO ceramic target (99.999%) located 5 cm away from the substrate surface. The films were grown at temperatures ranging from 350 to 1000 °C in 1×10^{-5} Torr of pure oxygen (99.9999%). The surface morphology of the substrates and films was imaged by contact-mode atomic force microscope (AFM). The crystallinity of the films was characterized by a high resolution x-ray diffraction apparatus equipped with a four-crystal monochromator and an analyzer crystal with resolutions of 0.005° and 0.008°, respectively. The electronic properties of the films were characterized at room temperature by Hall measurements (van der Pauw configuration) with indium ohmic electrodes.

Figure 2 shows AFM images for three kinds of substrates used in this study, i.e., as-polished sapphire(0001), as-polished, and cleaved ScAlMgO$_4$(0001), and those of the ZnO films grown on the respective substrates at 1000 °C. Here, we note that the as-polished ScAlMgO$_4$ surface has atomically flat terraces and 0.85 nm high steps, parallel in one direction [Fig. 2(c)]. This step height corresponds to one third of the *c*-axis length of ScAlMgO$_4$, i.e., a pair of wurtzite (MgAl)O$_x$ and rocksalt ScO$_y$ layers as schematically shown in Fig. 1. We presume that the appearance of such a well-defined surface structure is due to selective etching of one of the constituting layers during polishing in a solution, as in the case of SrTiO$_3$(100) etched in a weak acid.[9] The miscut angle of this particular substrate was deduced as 0.14° by taking into account the ratio of the step height to the average terrace width of 340 nm. When the substrate is cleaved along the (0001) plane, the surface shows a step-free and atomically flat area of about 100 μm in size. Apparently bunched steps seen by an optical microscope could be located in an AFM image as shown in Fig. 2(e).

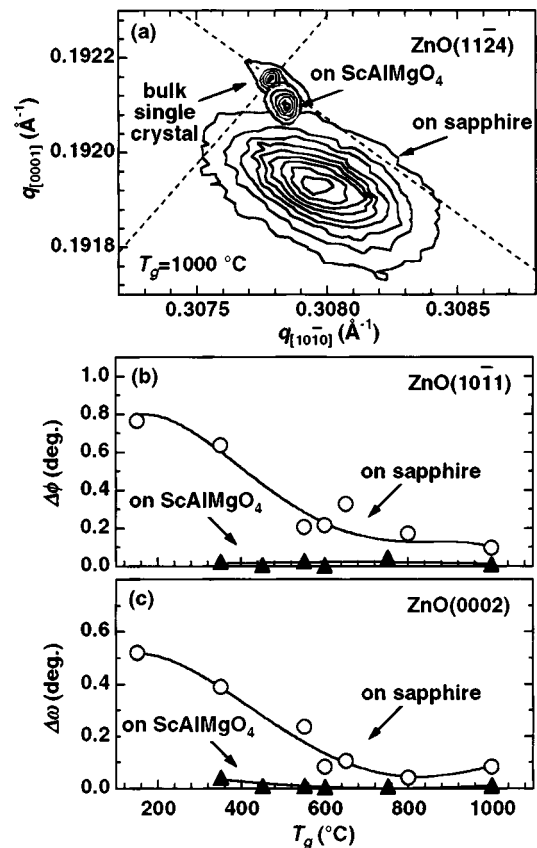FIG. 3. (a) Reciprocal space contour mapping of ZnO(11$\bar{2}$4) peaks for a bulk ZnO single crystal and the films grown on sapphire and ScAlMgO$_4$ at 1000 °C. Broken lines are guides for the eye for the directions of the Bragg diffraction and tilting. (b) and (c) Growth temperature dependence of the FWHM ($\Delta\phi$ and $\Delta\omega$), for in-plane and out-of-plane rocking curves measured for ZnO films grown on sapphire (○) and ScAlMgO$_4$ substrates (▲).

As can be clearly seen in Figs. 2(d) and 2(f), ZnO thin films grown on ScAlMgO$_4$ have very flat surfaces as represented by atomically flat terraces and an 0.26 nm high step (a charge neutral unit of ZnO). On the other hand, the film grown on sapphire [Fig. 2(b)] shows a much rougher surface than those on ScAlMgO$_4$, by 2 orders of magnitude. On the film grown on an as-polished substrate [Fig. 2(d)], many steps are aligned in one direction, suggesting step-flow growth mode. The tilting angle of the film surface from the (0001) basal plane was calculated to be 0.17°, which agrees with the miscut angle of the substrate within statistical error. On the cleaved substrates, the film grows in a two dimensional growth mode with a random nucleation, resulting in coaxially aligned and round shaped steps, Fig. 2(f).

The crystallinity is also drastically improved by using ScAlMgO$_4$ substrates. All the films grown on ScAlMgO$_4$ substrates showed an epitaxial relationship of ZnO(0001)//ScAlMgO$_4$(0001) and ZnO[11$\bar{2}$0]// ScAlMgO$_4$[11$\bar{2}$0] without any trace of the other in-plane orientation domains which were observed for ZnO/ sapphire(0001) (Ref. 10) (twisting by 30°) and GaN/ ScAlMgO$_4$ (Ref. 7) (twisting by 0.4°). Figure 3(a) shows reciprocal space mapping of ZnO(11$\bar{2}$4) peaks for a commercial bulk single crystal (Litton Airtron Co., Ltd.) and the films grown on ScAlMgO$_4$ and sapphire substrates at 1000 °C. Obviously, the diffraction peak of ZnO/ScAlMgO$_4$ is much sharper than that of ZnO/sapphire and has almost the
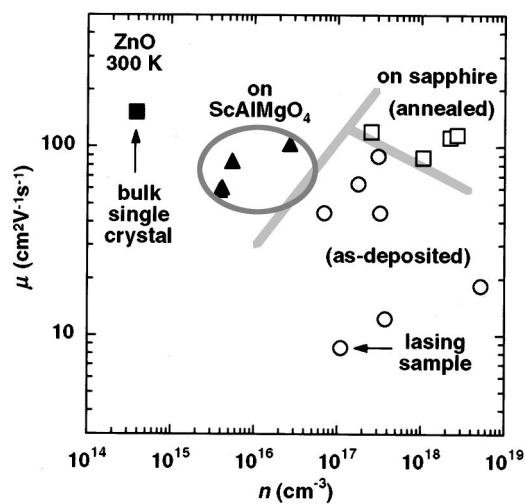
FIG. 4. Electronic properties of various undoped ZnO films and a bulk single crystal are mapped out in a plane of carrier concentration (n) and electron mobility (μ). Gray lines and circles show the boundaries classifying as-deposited ZnO/sapphire ($\bigcirc$), ZnO/sapphire annealed at 1000 °C in 1 atm of O_2 ($\square$), and as-deposited ZnO/ScAlMgO$_4$ ($\blacktriangle$).

same quality as that of the single crystal. The peak position shift of the films can be interpreted as due to the strain induced by the thermal expansion mismatch. The fluctuation of crystal orientation, i.e., in-plane *twisting* ($\Delta\phi$) and out-of-plane *tilting* ($\Delta\omega$) as represented by the full width at half maximum (FWHM) of the ($10\bar{1}1$) and (0002) rocking curves, is plotted as a function of growth temperature T_g in Figs. 3(b) and 3(c). The values of $\Delta\phi$ and $\Delta\omega$ for ZnO/ScAlMgO$_4$ grown above 450 °C are temperature independent and less than 0.02° and 0.01°, respectively, while a slight increase in the out-of-plane $\Delta\omega$ was detected only for the sample grown at 350 °C. When ZnO films were grown on sapphire, much larger $\Delta\phi$ and $\Delta\omega$ values were observed in the full temperature range. As T_g increased $\Delta\phi$ and $\Delta\omega$ decreased, but still remained larger than 0.09° and 0.04°, respectively. Therefore, we can conclude that ZnO thin films having comparable crystallinity to that of the bulk crystal can be grown even at a temperature as low as 400 °C.

The electronic properties of undoped films grown on various substrates were investigated by Hall measurements and summarized in Fig. 4. ZnO films grown on ScAlMgO$_4$ clearly showed both high μ (60–100 cm^2/V s) and low n ($0.4-2.7\times10^{16}$ cm^{-3}) when compared to the films grown on sapphire. We did not observe any considerable dependence of n and μ on T_g. In the case of ZnO/sapphire, the residual carrier concentration was as large as 10^{18} cm^{-3}. After these films were annealed at 1000 °C in 1 atm of oxygen to decrease grain boundary density, the values of μ increased, while the values of n showed no considerable change.[11] Therefore, it is concluded that the use of ScAlMgO$_4$ substrate is essential not only for improving the electron mobility by reducing crystalline defects, but also for reducing the residual carrier concentration. We have examined the doping capability of these high crystalline thin films by preparing n^{++}-type ZnO doped with Al by using 0.5% Al$_2$O$_3$ mixed ceramic target. These films showed high conductivity ($>10^3$ S cm^{-1}) and high crystallinity ($\Delta\phi$ and $\Delta\omega$ less than

0.05°). The doped films grown on sapphire substrates cannot achieve both requirements simultaneously because a higher growth temperature is needed to obtain a higher crystallinity, whereas lower temperature is needed to prevent segregation of Al$_2$O$_3$ and related compounds at grain boundaries.

We have also examined the optical properties of some of the films. Absorption spectra taken at 6 K for 50 nm thick films on ScAlMgO$_4$ showed a clear doublet in the exciton absorption peak, which can be assigned to A and B excitons separated by 7.0 meV. This splitting has not been observed so far for the films grown on sapphire because of the large nonradiative damping constant of excitons due to poor crystallinity, and also not for high quality bulk single crystals because of the large thickness. Those excellent optical properties enable us to estimate each excitonic parameter directly from the absorption spectra. We are also proceeding to characterize such optical properties as stimulated and laser emission under a strong excitation condition. The details will be published elsewhere.

In conclusion, the application of ScAlMgO$_4$(0001) substrates has substantially improved the crystalline quality of epitaxial ZnO thin films. We note a high surface smoothness, high crystallinity, excellent electronic properties such as low residual carrier concentration ($\sim10^{15}$ cm^{-3}) and high electron mobility (~100 cm^2/V s), a small damping constant of excitons observed in absorption spectra, and efficient n-type doping. These excellent properties of the films provide us the opportunity to fabricate sophisticated heterostructures and also possibly p-type ZnO.

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