Fabrication of wide-band-gap Mg$_x$Zn$_{1-x}$O quasi-ternary alloys by molecular-beam epitaxy

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A series of wurtzite MgZnO quasi-ternary alloys, which consist of wurtzite MgO/ZnO superlattices, were grown by molecular-beam epitaxy on sapphire substrates. By changing the thicknesses of ZnO layers and/or of MgO layers of the superlattice, the band-gap energy was artificially tuned from 3.30 to 4.65 eV. The highest band gap, consequently realized by the quasi-ternary alloy, was larger than that of the single MgZnO layer, we have ever reported, keeping the wurtzite structure. The band gap of quasi-ternary alloys was well analyzed by the Kronig–Penny model supposing the effective masses of wurtzite MgO as $0.30m_0$ and $(1-2)m_0$ for electrons and holes, respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.1923762]

Zinc oxide (ZnO) and related semiconductor crystals have recently attracted increasing interest toward application to ultraviolet (UV) light emitters,[1] deep UV sensors,[2] transparent thin-film transitors,[3] multifunctional integrated circuits, and so on. For the actual device applications, the band-gap engineering is one of the indispensable issues to be achieved, for example, the alloying with magnesium oxide (MgO) to make MgZnO can increase the band-gap energy from 3.3 eV for wurtzite ZnO to 7.8 eV for rocksolt MgO (Ref. 4) with fairly small mismatching (0.1%) (Ref. 5) in bond lengths of ZnO and MgO.

However, in a lot of research on the growth of MgZnO, one encounters the fatal problem of phase separation,[6,7] where a segregated nanophase embedded in the host matrix is precipitated.[8] Accordingly, in the previous works, the maximum band gap extended from ZnO and achieved with wurtzite MgZnO has been limited to 3.9 eV.[6,7] For that problem, we have recently proposed the use of a high-quality ZnO buffer layer to firmly fix the crystal structure of the layer successively grown on it to wurtzite and, as a result, the growth of single-phase wurtzite Mg$_x$Zn$_{1-x}$O with magnesium (Mg) content x of as high as 0.51 with band-gap energy of 4.45 eV has been reported.[9]

In the present letter, the attempt to realize the wider band gap, as well as to easily and widely control the band gap, is reported by the use of MgO/ZnO superlattice quasi-ternary alloys, instead of MgZnO ternary alloys. A quasi-ternary alloy of AX and BX layers (A and B are cation, X is anion) or of YC and YD layers (Y is cation, C and D are cation) consists of AX/BX or YC/YD superlattices, which is recognized equivalent to a ternary alloy A$_x$B$_{1-x}$X or YC$_x$D$_{1-x}$ from the view point of the band-gap energy. One of the advantages of quasi-alloys[10–16] is that their band gap can be tuned by the thicknesses of the constituent binary layers, allowing easy modulation of band gap energy along the growth direction. Further, one may not encounter any problem arising from *alloying*, such as phase separation or alloy scattering. Therefore, by the MgO/ZnO superlattice quasi-ternary alloy, one may expect the possibility of extending the band-gap energy over 4.45 eV attained by the single MgZnO layer. Actually, in the present work, we report the quasi-ternary alloy with its band gap of as large as 4.65 eV, which is wide band gap realized with a wurtzite ZnO-based semiconductor.

The motivation for the MgO/ZnO superlattice quasi-ternary alloys is supported by the fact that a thin wurtzite MgO layer can be grown on a wurtzite ZnO layer. We employed molecular beam epitaxy (MBE) for the growth on a-plane (11$\bar{2}$0) sapphire substrates using solid sources of zinc (Zn) and magnesium (Mg) together with rf radical oxygen source. Details of the growth system and process have been published elsewhere.[17] Following the cleaning of substrate surface in the MBE growth chamber, a ZnO buffer layer was grown at 390 °C, then it was annealed at 710 °C without irradiation of any source for the improvement of both the crystallinity and surface morphology. Figure 1 shows the reflection high-energy reflection (RHEED) pattern when a MgO layer is grown on the ZnO buffer layer at 490 °C, where the growth rate of MgO was about 4 nm/min. The oxygen flow rate and rf power of the radical cell were kept at 0.30 sccm and 400 W, respectively. The

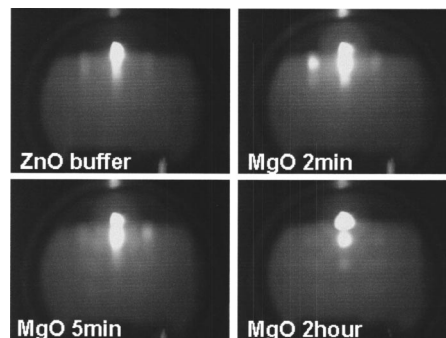FIG. 1. Variation of RHEED patterns of MgO on a ZnO buffer layer with the growth time. The growth rate of MgO was about 4 nm/min.

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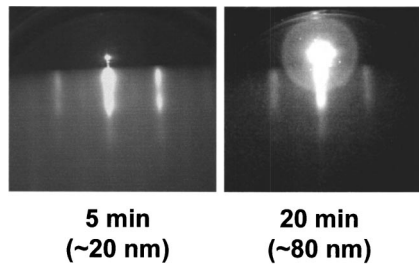
FIG. 2. RHEED patterns of a MgZnO quasi-ternary alloy during the growth, that is, 5 min (about 20 nm) and 20 min (about 80 nm) after starting the growth, showing wurtzite structure throughout the growth.

FIG. 4. An example of optical transmission spectrum of a MgZnO quasi-ternary alloy with wide band gap, in comparison to that of the MgZnO single layer of wurtzite structure and possessing the highest band-gap energy of 4.45 eV.

beam pressures of Zn and Mg were at about 2×10^{-6} Torr and 2×10^{-7} Torr, respectively.

As shown in Fig. 1, after starting the growth of MgO on ZnO, no significant change in the RHEED pattern was found until the growth time of 2 min (about 8 nm in thickness). However, as the growth proceeded, it changed the spotty one, suggesting severe degradation and/or incorporation of the rocksalt structure. This implies that the MgO on ZnO takes a wurtzite structure until its thickness exceeds a critical value.

Therefore, it could be possible to fabricate MgO/ZnO superlattice quasi-ternary alloys, keeping the wurtzite structure, by limiting the thickness of the MgO below the critical one, for example, <10 nm. Figure 2 shows the RHEED patterns during the growth of a MgO/ZnO superlattice. The streaky pattern, suggesting wurtzite structure, was continuously seen throughout the growth.

The MgO/ZnO superlattice structure was characterized by transmission electron microscopy (TEM). Figure 3 shows the dark-field TEM image of one of the superlattices. The striped structure of the superlattice of 60 periods, as we designed, with the thickness of each constituent layer of about 1 nm was confirmed. This implies that Zn and Mg atoms hardly diffuse each other to form the short-period superlattice acting as a quasi-ternary alloy. However, in Fig. 3, many dislocations and thickness fluctuation of the constituent layers are present. It may be due to the unoptimized structure design and growth conditions, at present.

The band gap of the MgZnO quasi-ternary alloys was determined from the transmission spectra of the films. An example of the spectrum, in comparison with that of a single MgZnO layer, whose thickness is about 650 nm, is shown in Fig. 4. Calculating the band gaps from the spectra, it is shown that the arbitral tuning of the band-gap energies from 3.30 to 4.65 eV is achieved by changing the thicknesses of
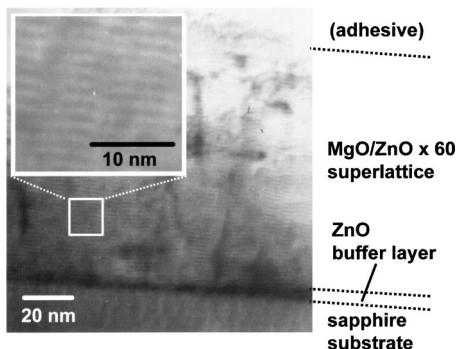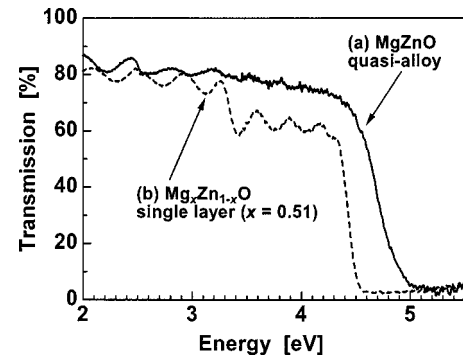
ZnO and MgO layers. The maximum band gap attained was 4.65 eV, which is higher than our previous achievement with a wurtzite $Mg_{0.51}Zn_{0.49}O$ single layer.[9] It should be noted that in Fig. 4, the spectra near the absorption edges of MgZnO quasi-ternary alloys are not steep in comparison with the MgZnO single layers. One of the reasons may be the fluctuation of the layer thicknesses, as suggested from the TEM result shown in Fig. 3.

The x-ray diffraction (XRD) $\theta - 2\theta$ spectra of the quasi-ternary alloys and the MgZnO single layer are depicted in Fig. 5. For the quasi-ternary alloys with the band gap 3.30 to 4.65 eV, only the peaks similar to the (0002) peak from the wurtzite MgZnO were observed, suggesting that the MgZnO quasi-ternary alloys keep the wurtzite structure. The peak position slightly shifts to a higher degree with the increase of the average Mg content in the quasi-ternary alloys.

Then, attempts will be given to analyze the band gap energy values, obtained from the optical transmission measurement, by the theoretical calculation based on the Kronig-Penny model. As a fundamental parameter for the calculation, the valence-band offset at the MgO/ZnO interface must be determined. Ultraviolet photoelectron spectroscopy (UPS) is a useful tool for this purpose, but the clear signal was not obtained from the wurtzite MgO/ZnO structure because the MgO layer was too thin. Therefore, we prepared the series of $Mg_xZn_{1-x}O$ single layers with x of 0, 0.20, and 0.40, and

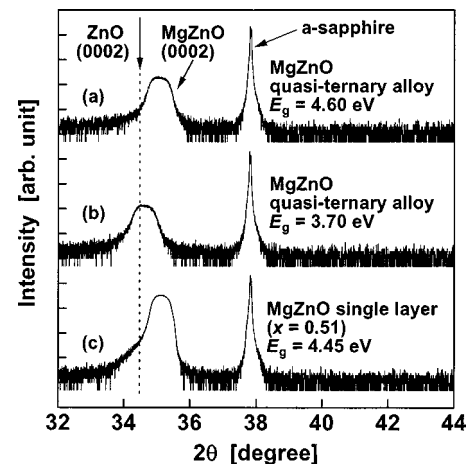FIG. 3. Cross-sectional TEM images of a MgZnO quasi-ternary alloy with a (MgO/ZnO×60 superlattice.

FIG. 5. XRD $\theta - 2\theta$ spectra of MgZnO quasi-ternary alloys, in comparison to that of the MgZnO single layer of wurtzite structure and possessing the highest band-gap energy of 4.45 eV.

TABLE I. Structures of MgO/ZnO superlattices and their band gaps determined from optical transmission spectra. The theoretical values of the band gaps calculated by using the Kronig–Penny model under the assumption of the band offset at MgO/ZnO as 1.22 eV and the effective masses of wurtzite MgO as $0.30m_0$ for electrons and $(1-2)m_0$ for holes are also shown in the table for comparison.

MgO (nm)	ZnO (nm)	Bandgap (eV) (measured)	Bandgap (eV) (calculated)
0.20	0.20	3.65	3.45
0.50	0.50	3.60	3.66
0.90	0.90	3.50	3.57
1.0	0.27	4.15	4.18
1.5	0.27	4.60	4.63
4.0	0.90	4.60	4.63
6.0	1.3	3.70	3.69

they are subjected to the UPS measurement. The result gives the energy position of valence-band maximum as a function of x, and by extrapolating the results to $x=1$, the valence-band maximum of wurtzite MgO was estimated. Comparing the values hence obtained, the band offset at MgO/ZnO interface was estimated to be 1.22 eV. On the other hand, as a result of tight-binding approach proposed by Harrison,[11,12] the value of the valence-band offset was calculated to be only 30 meV. It is thought that this difference is due to the effects of cation d orbital. These effects were neglected in the references.[18,19] Wei and Zunger[20,21] pointed out that p^a-d^c interaction could not be neglected in compound semiconductors, especially in II-VI compounds. It is thought that the valence-band maximum of ZnO is shifted upward by the p-d repulsion and it is thought that the estimated valence-band offset value of 1.22 eV from UPS is due to this effect. Then, the conduction-band offset is calculated to be 1.75 eV by taking the band gaps of wurtzite ZnO and MgO as 3.37 eV and 6.34 eV, respectively.[22] With the use of above values, the subband energies E were derived by using the Kronig–Penny model.

It should be noted that the calculation needs the effective masses in ZnO and MgO. For ZnO, we used $0.30m_0$ and $1.8m_0$ as the effective masses of electrons and holes,[23] respectively. However, the effective masses of wurtzite MgO have been ambiguous so far. Therefore, we treated the effective masses of MgO as fitting parameters and the band gaps of various MgO/ZnO superlattice structures have been analyzed by using the above equations. As a result, the theoretical values of the band gaps well coincided with the experimental values in various structure samples, when the effective masses of electrons and holes in wurtzite MgO were assumed to be $0.30m_0$ and $(1-2)m_0$, respectively. Since the critical relationship between band offsets and effective masses is mainly seen for relatively light masses, for example, $<0.5m_0$, the effective mass of holes cannot be obtained more accurately than $(1-2)m_0$. The results are summarized in Table I.

In summary, we reported the fabrication of wurtzite Mg-ZnO quasi-ternary alloys by applying MgO/ZnO short-period superlattices. The band gaps were tuned from 3.30 to as large as 4.65 eV, which was larger than that achieved by the wurtzite MgZnO single layer, and were well explained by the Kronig–Penny model using the band offset at MgO/ZnO as 1.22 eV and the effective masses of wurtzite MgO as $0.30m_0$ for electrons and $(1-2)m_0$ for holes. Using these MgZnO quasi-ternary alloys, it is expected to become easier to design the various and unique ZnO-based semiconductor devices.

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