I. INTRODUCTION

Wide-band-gap ZnO has attracted attention in research as an alternative material to GaN for the fabrication of exciton-based laser diodes and light-emitting diodes, since it has the largest exciton and biexciton binding energies in the semiconductor material’s family. It has been demonstrated that the exciton binding energies and band-gap energy in epitaxial ZnO layers can be engineered by quantum confinement. Epitaxial ZnO has been alloyed with MgO for a Mg content of 40%, while the band-gap energy was engineered to 4.0 eV. In those studies, the Mg composition was determined by employing chemical techniques, such as sputtered ion-mass spectroscopy, secondary ion-mass spectroscopy, and inductively coupled plasma-mass spectroscopy (ICPS). These experimental techniques are truly insensitive to the physical state of strain and bowing parameters of heterostructures. These physical parameters, in principle, play crucial roles in epitaxy and control the quality of heterostructures.

A routine determination of alloy composition by employing Vegard’s law can properly account for the sample’s state of strain. The use of Vegard’s law in II-VI oxide (II-O) materials, however, requires standard MgO and ZnO lattice constants along the a and c axes. There has been a theoretical study of the lattice constant of wurtzite MgO material along the a axis of 3.199 Å with a c/a ratio of 1.633. This leads $c_{\text{MgO}}$ to be 5.224 Å, greater than that of $c_{\text{ZnO}}$ (5.086 Å). However, with an increase of Mg composition in the Mg$_x$Zn$_{1-x}$O alloy, the $c_{\text{MgO}}$ axis length decreases, indicating that the $c_{\text{MgO}}$ has to be less than the $c_{\text{ZnO}}$ ratio. Therefore, the theoretical calculation may need to be reconsidered for the exact values of the c/a ratio and the lattice constant of the MgO material.

In this article, $c_{\text{MgO}}$ and $a_{\text{MgO}}$ lengths have been assigned to 5.086 Å and 3.199 Å, respectively, that have been presented in Table I. Using Vegard’s law, the Mg composition in Mg$_x$Zn$_{1-x}$O alloys has been estimated to be from 0 to 56%, which is consistent with results of other studies. The lattice constants in Mg$_x$Zn$_{1-x}$O alloys as a function of Mg composition determined by employing Vegard’s law and a theoretical model showed an error limit of ~3%. The photon energies of Mg$_x$Zn$_{1-x}$O alloys do not follow Vegard’s law and the localized exciton ($D^0X$) disappeared completely in the photoluminescence (PL) spectra, while the neutral donor-acceptor pair ($A^0X$) and 1-longitudinal optical-phonon energies decreased rapidly with increasing Mg content. These asymmetric behaviors in the Mg$_x$Zn$_{1-x}$O alloys are the subject of locally disordered Mg potential fluctuations and an artifact of the $c_{\text{MgO}}$ and $a_{\text{MgO}}$ lengths calculated theoretically.

II. EXPERIMENT

Mg$_x$Zn$_{1-x}$O alloys were grown directly on 6H–SiC(0001) substrates by metalorganic chemical-vapor deposition. The substrate cleaning and processing have been described in detail elsewhere. For the growth of Mg$_x$Zn$_{1-x}$O layers, the flow rates of diethyl zinc (DEZn) and bismethyl cyclopentadienyl-magnesium [(MeCp)$_2$Mg] were controlled by adjusting the flow rate of the carrier gas N$_2$. The substrate temperature was then increased to the selected temperature of 475 °C for the successive growth of Mg$_x$Zn$_{1-x}$O layers. DEZn and (MeCp)$_2$Mg were allowed to flow first for ~20 s, and then O$_2$ was introduced. In these Mg$_x$Zn$_{1-x}$O alloys, the flow rates of (MeCp)$_2$Mg and O$_2$ were kept constant at 20
and 10 sccm, respectively, while the flow rate of DEZn was varied from 0 to 12 sccm. The typical Mg$_{1-x}$Zn$_x$O layer thickness was 0.5 μm.

For determination of the Zn and Mg contents, MgZnO samples were dissolved in concentrated HNO$_3$ followed by ICPS analysis. The ICPS system is considered a sequential multielement analyzer that has scan times less than 20 ms for one sweep. The signal intensity is a function of the number of analytic ions in the plasma and the mass-dependent transport through the mass spectrometer. Determination of Zn and Mg was performed with a Shimadzu ICPS-1000IV spectrophotometer.

### III. RESULTS AND DISCUSSION

To justify the study of the Mg$_{1-x}$Zn$_x$O alloy, an overview of epitaxial ZnO layers deposited on 6H–SiC substrates is briefly discussed. The ZnO layers exhibited virtually relaxed lattice constants along the $a$ and $c$ axes of 3.246 and 5.205 Å, respectively. With these lattice constants, the dominant $D^0$X was recorded to be 3.364 eV at 4 K.

Figure 1 shows the x-ray diffraction (XRD) patterns obtained from Mg$_{1-x}$Zn$_x$O layers deposited on 6H–SiC substrates. It is noted that all of the Mg$_{1-x}$Zn$_x$O layers orient along the (002) and (205) planes, which correspond to symmetric and asymmetric peaks. It is evident that these XRD peaks shift systematically: The (002) peak positions shifted to higher angles, while the (205) peak positions shifted to lower angles with increasing Mg content. The out-of-plane lattice constant of the Mg$_{1-x}$Zn$_x$O layers was calculated using Bragg’s law for the (002) plane by $n\lambda = 2d \sin \theta$, where, $\lambda$ and $d$ are the x-ray wavelength and the diffracted lattice constant, respectively. However, for the asymmetric (205) planes of Mg$_{1-x}$Zn$_x$O alloys with the first-order approximation ($n=1$), Bragg’s law can be written as

$$\sin \theta = \frac{\lambda}{2} \sqrt{\frac{16}{3a^2} + \frac{25}{c^2}}. \quad (1)$$

Using Eq. (1), the $c$-axis and $a$-axis lengths were estimated for the relative $c$-axis lengths calculated from the (002) planes.

A systematic study of the $c$-axis and $a$-axis lengths as a function of Mg composition were determined and plotted in Fig. 2. For the comparative studies, the Mg$_{1-x}$Zn$_x$O/Al$_2$O$_3$ film parameters are plotted together with the Mg$_{1-x}$Zn$_x$O/6H–SiC heterostructure, cited from Ref. 3. The $c$-axis length decreases, while the $a$-axis length increases with the increase of Mg composition in Mg$_{1-x}$Zn$_x$O layers grown on 6H–SiC and Al$_2$O$_3$ substrates. It is clear that the $c$-axis and $a$-axis lengths are consistent in these heterostructures for composition where the Mg content is <30%. For the Mg$_{1-x}$Zn$_x$O/6H–SiC heterostructure, however, the fitted results of $c$-axis and $a$-axis lengths are found to be 5.2042 ± 0.072x and 3.2491 ± 0.047x, respectively. It reveals that the $c$-axis length decreases 1.5 times faster than the $a$-axis length, i.e., the $c$-axis length of Mg$_{1-x}$Zn$_x$O alloys shrinks rapidly, and agrees well with the known fact that the $c$-axis length should be less than that of the $c_{ZnO}$.
The accuracy of Mg composition determination using Bragg’s and Vegard’s laws can be verified by using the theoretical model calculation. For an ideal ZnO crystal, the distance ($R_{\text{ZnO}}$) between two neighboring Zn and O atoms can be written as $R_{\text{ZnO}} = r_{\text{Zn}} + r_{\text{O}}$, where $r_{\text{Zn}}$ (0.60 Å) and $r_{\text{O}}$ (1.38 Å) are Pauli covalent radii of Zn and O atoms, respectively. Assuming a variation in $R_{\text{ZnO}}$ due to the kinetics of neighboring atoms, the elastic strain $e_{\text{es}}$ in the (001) direction will be $e_{\text{es}} = \Delta R_{\text{ZnO}} / R_{\text{ZnO}}$.

For an ideal MgZnO solid solution, in principle, a Mg ($r_{\text{Mg}} = 0.57$ Å) atom occupies a substitutional Zn site. Therefore, the strain $e_{\text{es}}$ in the (001) direction due to Mg atom incorporation becomes $e_{\text{es}} = \Delta R_{\text{ZnO}} / R_{\text{ZnO}} = (r_{\text{Zn}} - r_{\text{Mg}}) / (r_{\text{Zn}} + r_{\text{O}}) \times x$, where $x$ is the Mg composition in Mg$_x$Zn$_{1-x}$O alloy. Hence, the lattice constant variation due to Mg atom incorporation into the Mg$_x$Zn$_{1-x}$O layers can be written as

$$\Delta d_{\text{ZnO}} = d_{\text{ZnO}} \frac{C_{11} + 2C_{12}r_{\text{Zn}} - r_{\text{Mg}}}{C_{11} r_{\text{Zn}} + r_{\text{O}}} \times x,$$

where $C_{11}$ and $C_{12}$ are the elastic stiffness constants plotted in Table I.

Figure 3(a) shows the calculated dependence (○) of $c_{\text{MgZnO}}$ axis length in Mg$_x$Zn$_{1-x}$O alloys as a function of Mg composition using the simplified model [Eq. (2)] together with the XRD data. The physical parameters used in these calculations are plotted in Table I. The model calculation indicated that the $c_{\text{MgZnO}}$ axis length decreases monotonically, while the $c_{\text{MgZnO}}$ axis length is almost linear with the increase of Mg composition when estimated by Vegard’s law. The maximum error in lattice constants calculated from the simplified model (2) and Vegard’s law is $\sim 3\%$. This uncertainty has been attributed to the large lattice misfit in the ZnO/MgO materials system of $\sim 2\%$. Neugebauer et al. reported that the atomic relaxation in such a large lattice mismatch material system is of great significance to the lattice property. This suggests that the $\sim 3\%$ discrepancy between this simplified model and Vegard’s law comes from the atomic relaxation.

The Mg compositions in Mg$_x$Zn$_{1-x}$O/6H–SiC heterostructures were also determined experimentally by ICPS, which are almost consistent with the Vegard’s law plotted in Fig. 3(b). The fluctuation of Mg content is marked between the Vegard’s law and ICPS experimental results. This fluctuation may be contributed due to the theoretically calculated $c_{\text{MgO}}$ axis length based on the $c/a$ approximation of 1.59 and/or Mg incorporation in interstitial or antisites of the ZnO lattices.

Figure 4 shows selective Mg composition-dependent PL spectra dominated by $D^\text{X}$, neutral donor-acceptor pair ($A^0\text{X}$), and 1LO-phonon bands. The details of the PL prop-
properties will be reported elsewhere. With the increase in Mg content from 0 to 40% that has been determined by employing Vegard’s law, the $D^0X$ band energy is blueshifted by $\sim 0.6$ eV. The systematic Mg composition-dependent band energies of Mg$_x$Zn$_{1-x}$O layers are plotted in the inset of Fig. 4. The $D^0X$, $A^0X$, and 1LO-phonon energies increase slowly with the increasing Mg composition for $x < 30\%$. However, for the higher Mg composition ($x > 30\%$), the $D^0X$ peak disappeared in the PL spectra, while the $A^0X$ and 1LO-phonon bands energies decrease rapidly. We attempted to fit these PL data but these do not follow the Vegard’s law. These nonlinear and asymmetric behaviors for $D^0X$, $A^0X$, and 1LO-phonon require further studies for clarification.

While the PL properties do not satisfy Vegard’s law, the structural properties comply with both Bragg’s and Vegard’s laws. However, the transmission and reflectance measurements, together with the PL, can give insight into the details of these optical properties. Critical investigations of these properties in Mg$_x$Zn$_{1-x}$O layers are under way, and the studies will be reported elsewhere. However, it is expected that the inhomogeneous Mg incorporation microscopically in Mg$_x$Zn$_{1-x}$O layers may have an active role that has made a contradiction between the structural and optical properties, although a rather homogeneous alloying is expected due to the similar tetrahedral ionic radius of Mg$^{2+}$ and Zn$^{2+}$ to 0.57 Å. This work was supported in part by the Special Postdoctoral Research Fellowship Program, Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), Japan.

IV. CONCLUSION

Ternary Mg$_x$Zn$_{1-x}$O material has been deposited on 6H-SiC substrates for the Mg composition of 0–56%. The Mg compositions determined by ICPS and Vegard’s law fluctuated for 5–8%, while the $c_{\text{MgZnO}}$ length estimated by Vegard’s law and ICPS showed an uncertainty of $\sim 3\%$. It was found that the $c_{\text{MgZnO}}$-axis length decreases 1.5 times faster than does the $d_{\text{MgZnO}}$-axis length. It was also found that the photon energies of the Mg$_x$Zn$_{1-x}$O alloy do not comply with Vegard’s law. Although the structural properties of Mg$_x$Zn$_{1-x}$O alloy follow Vegard’s law, no clear conclusion was found for optical properties for validity of Vegard’s law.

ACKNOWLEDGMENT

This work was supported in part by the Special Postdoctoral Research Fellowship Program, Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), Japan.


