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The formation of a rock-salt type ZnO thin film by low-level alloying with MgO

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Abstract

A high pressure form of ZnO with a rock-salt structure can be synthesized as a thin film by a pulsed laser deposition technique when ≥ 15 mol% of MgO is alloyed. The phase is identified both by x-ray diffraction and near edge x-ray absorption fine structure (NEXAFS) measurements. NEXAFS is interpreted with the aid of first principles calculations employing a supercell composed of 108 atoms with a Zn-1s core-hole. The rock-salt phase can be formed only when an MgO(100) substrate is used because of a favourable lattice matching. As a result of the heteroepitaxy, the crystal is distorted tetragonally by $c/a = 1.02$. The energy increase due to the tetragonal deformation is estimated to be 2 meV/ZnO by a first principles calculation.

Zinc oxide (ZnO) has been widely studied because of its usefulness in optoelectronic applications, catalysis, chemical sensors, etc. It is known to crystallize in the wurzite (W) structure under ordinary conditions. Two other phases are known to be existent. A zinc blende (ZB) phase can be synthesized when a special processing route is chosen. For example, thin film processes using GaAs substrates with ZnS buffer layers [1] or Pt/Ti/SiO₂/Si substrates [2] succeeded in the formation of ZB. Ultrafine ZB particles were produced by a novel oxidation technique of Zn powders [3]. The ZB phase is often referred to as ‘cubic-ZnO’. This name is misleading since another cubic phase having a rock-salt (RS) structure can be synthesized under high pressure above 10 GPa at room temperature or above 6 GPa at 1200 K [4]. The RS phase is difficult to retain under ordinary conditions. It normally transforms back to W phase at 2 GPa at room temperature [1]. Retention of the RS phase from high pressure to ambient

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conditions has occasionally been successful [5–7]. However, no success in growing RS thin films has been reported to the authors' best knowledge.

Recently, extensive experiments to alloy ZnO with MgO have been reported, aiming to expand the bandgap [8–15] to the ultraviolet region. A pseudo-binary phase diagram of W-ZnO with RS-MgO has been established [16, 17]. The solid solubility of MgO in W-ZnO is 4 mol% under thermal equilibrium at 1573 K and 0.1 MPa. When grown as a thin film via a pulsed laser deposition (PLD) method, the solubility of MgO in W phase was reported to increase up to 33 mol% [8]. On the other hand, the stability of RS phase at 0.1 MPa has been reported to be ≥ 60 mol% MgO or $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with $x \geq 0.6$ [17]. We have recently demonstrated that the solubility range of the RS phase increases significantly under external high pressures via a combined study of systematic high pressure experiments and first principles calculations [18]. Under 4 GPa, the stability range became $x \geq 0.3$; x became zero under 6.5 GPa. In other words, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ shows single RS phase under any compositions when the external pressure is ≥ 6.5 GPa. RS phase with $x \geq 0.2$ was able to be retained at ambient conditions from high pressure and high temperature conditions.

A smaller increase in solubility of RS phase has been reported in a thin film. A maximum solubility of $x = 0.5$ has been reported for RS-ZnO via a PLD method [12]. The fabrication of RS- $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ /cubic-MgO multilayer thin films with $x = 0.5$ has been reported [19]. No works have reported the synthesis of RS- $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films with lower x .

In the present study, we aimed at the synthesis of RS- $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with lowest x by a thin film process via optimization of process conditions. The prime candidate for substrate is an MgO single crystal that has 1.6% smaller lattice constant than that of the RS-ZnO [12]. RS-ZnO on an MgO substrate can be expected to provide a compressive force in a lateral direction when hetero-epitaxially grown, which may expand the stability of the RS phase. MgO was chosen as an alloying element to stabilize the RS phase. Our first principles calculation by the plane-wave pseudopotentials method found that the theoretical transition pressure decreases from 12.7 to 10.2 GPa by alloying 12.5% of MgO with ZnO.

The ZnO:MgO films were prepared by a pulsed laser deposition (PLD) method using an excimer KrF* laser source ($\lambda = 248$ nm, $\tau = 25$ ns, Lambda Physik COMPEX205). The laser power was approximately 3×10^4 J m⁻². Two starting powders of fixed compositions were mixed using a magnetic stirrer in ethanol until they dried up. The mixed powders were then sintered at 1623 K in air to be used as PLD targets. All PLD experiments were done in an oxygen backfill pressure of $p_{\text{O}_2} = 0.1$ Pa. Other process variables were the substrate material and its crystallographic orientation, substrate temperature, and pulsed laser frequency.

It should be noted that the composition of the PLD film is not always the same as that of the target. According to Choopun *et al* [12], Zn-related species have a higher vapour pressure and thereby are easily desorbed at higher growth temperature during the PLD of ZnO–MgO. They found that the composition of MgO increases almost linearly with the substrate temperature, although the film grown at room temperature has a composition very close to the target. In the present study, the composition was determined via energy dispersive x-ray analysis (EDS) of the film using a scanning electron microscopy on films deposited on glassy SiO₂ substrates simultaneously with the specimens.

Prior to alloying experiments, undoped ZnO film was deposited on four different kinds of substrates, i.e., MgO(100), MgO(110), Al₂O₃(0001), and glassy SiO₂. The formation of crystalline phases other than the W structure was not evident by the x-ray diffraction (XRD) independent of the process conditions.

The RS structure can be found when a target with 90 mol% ZnO–10 mol% MgO and a MgO(100) substrate was used. Deposition was made at 373 K, and a 1 Hz laser was irradiated for 2000 shots. The thickness of the film was measured by a contact method to be 50 nm. x

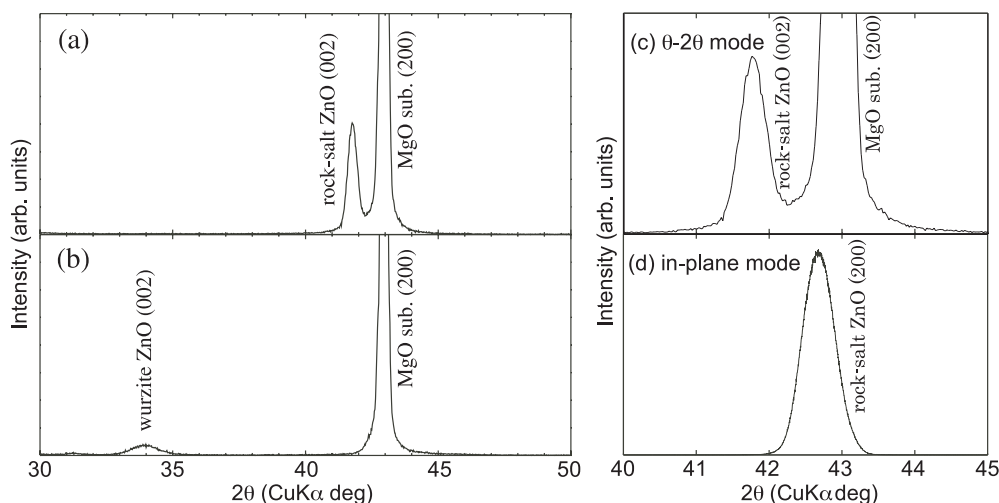


Figure 1. (a) and (b) X-ray diffraction pattern by nearly θ - 2θ scan for (a) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ film grown on $\text{MgO}(001)$ substrate, and (b) ZnO film grown with otherwise the same conditions as (a). (c) A close-up of (a). (d) The diffraction pattern obtained by the in-plane mode for $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$.

was determined by EDS after the deposition to be 0.15. Figures 1(a)–(c) show XRD patterns of the film using $\text{Cu K}\alpha$ radiation for $x = 0.15$ and 0 with nearly θ - 2θ scan. In order to avoid an intense diffracted beam from the substrate, the θ angle was offset by 0.15° . The film can be clearly distinguished from the MgO substrate when $x = 0.15$. No sign of W phase can be found by XRD. On the other hand, not a peak but a broad diffraction peak from the W phase can be found for $x = 0$. $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with $x = 0.15$ was also deposited on $\text{MgO}(110)$, $\text{Al}_2\text{O}_3(0001)$, and glassy SiO_2 . None of them showed the presence of the RS structure.

In-plane XRD using a grazing angle incident beam was carried out. As can be seen in figure 1(d), no contribution from the MgO substrate can be found in the in-plane mode. Combining the information, the film of $x = 0.15$ can be assigned to the RS structure with a small tetragonal distortion. The lattice parameters were determined to be $a = b = 4.24 \text{ \AA}$, $c = 4.33 \text{ \AA}$ and $c/a = 1.02$. The lattice parameters of the RS phase of MgO and ZnO under ambient conditions were reported to be 4.211 and 4.28 \AA , respectively. Assuming a linear relationship between the lattice parameter and the atomic fraction of alloying elements, i.e., Vegard's law, the lattice parameter of the RS- $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x = 0.15$) is 4.270 \AA . The lattice volume of the tetragonally distorted RS phase is 99.8% of that of the cubic-RS as determined by Vegard's law.

In order to examine the local atomic arrangement of Zn atoms in the film, near edge x-ray absorption fine structure (NEXAFS) was measured at the Zn K edge. NEXAFS was obtained at BL01B1 of SPring-8 with a bending magnet system with two mirrors and a fixed-exit double crystal monochromator utilizing $\text{Si}(311)$ planes. X-ray fluorescence from the sample was detected by a 19-elements Ge solid-state detector. All measurements were done in air at room temperature with two kinds of geometries, i.e., $\mathbf{E} \parallel \mathbf{T}$ and $\mathbf{E} \perp \mathbf{T}$, where \mathbf{E} is the electric field vector and \mathbf{T} is the vector perpendicular to the thin film.

Figure 2 shows the experimental NEXAFS of the present RS film in comparison with that of W film. The spectrum of the RS is composed of three peaks denoted by A, B and C. The spectral shape is clearly different from that of W showing four peaks, denoted by a to d. A small but reproducible difference in the position of peak B and relative height of peaks A and

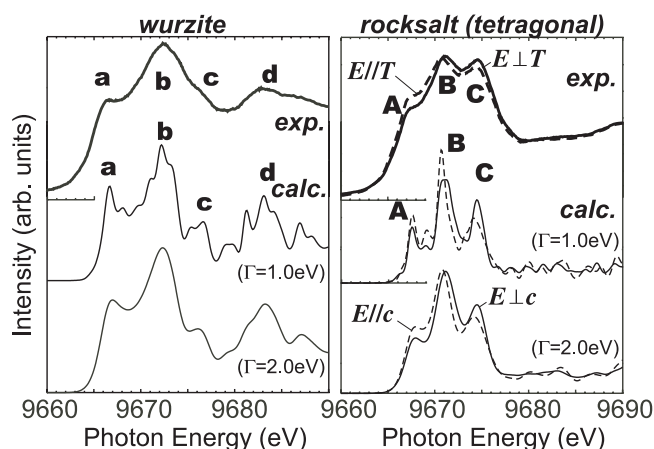


Figure 2. Experimental and theoretical near edge x-ray absorption fine structures from W-ZnO powder and the rock-salt type $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ thin film showing tetragonal distortion.

C can be seen between the two orientations. Since no experimental spectrum on NEXAFS of RS-ZnO was available, we made first principles calculations to obtain theoretical spectra for the two phases. Calculations were made by the orthogonalized linear combination of the atomic orbital (OLCAO) method [20] using a local density approximation and atomic orbital basis functions. This method has been successful for reproducing a number of experimental NEXAFS of many kinds of compounds [20–23]. In order to reduce interactions among core-holes, large supercells composed of 108 atoms were adopted for both RS and W. Experimental lattice constants were used. The initial state (ground state) and final state (core-holed state) were calculated separately. The core-hole was included in a Zn-1s orbital. The matrix elements of the electric dipole transition between the initial and final states were rigorously computed using wavefunctions at the two states. Theoretical NEXAFS were made by broadening the theoretical spectra with Gaussian functions of $\Gamma = 1.0$ and 2.0 eV full width at half maximum. The theoretical transition energy was obtained as the total energy difference between the final and the initial states. The theoretical spectrum of W-ZnO satisfactorily reproduced the experimental spectra when the absolute transition energy was shifted by $+72.5$ eV ($\Delta E/E = 0.75\%$) and $\Gamma = 2.0$ eV. The theoretical spectra of RS-ZnO with tetragonal lattice constants ($c/a = 1.02$) also satisfactorily reproduced the experimental spectra assuming T is parallel to the c -axis of the tetragonal phase. The agreement in the spectral shape clearly confirms that Zn atoms are incorporated in the RS phase with tetragonal distortion. Our analyses of the partial density of states found that all peaks as denoted by A to C and a to d originate mainly from Zn-4p orbitals which are hybridized with Zn-4s and 4d orbitals in different manners. However, a more detailed analysis on the origin of these peaks is beyond the scope of the present study.

In order to examine the energetics of the tetragonal structure, first principles calculations were made by a plane-wave pseudopotentials method using a code CASTEP [24]. Ultrasoft pseudopotentials and plane-wave cutoff energies of 500 eV were chosen. A generalized gradient approximation was used to take account of the exchange–correlation term. First the crystal structures were optimized with an orthogonal lattice with $Cmcm$ space group and an arbitrary set of initial atomic arrangements that is allowed by the symmetry. We then found that the presence of space groups with lower symmetry than the tetragonal $I4/mmm$ cannot be significant within the accuracy of the present computation.

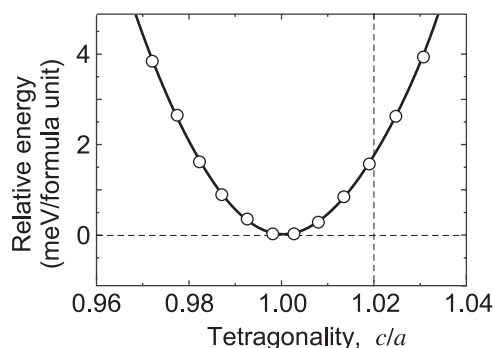


Figure 3. Total energy as a function of tetragonality, c/a , by first principles plane-wave pseudopotential calculations for RS-ZnO with space group $I4/mmm$. The energy is relative to that of the cubic rock-salt phase, i.e., $c = a$.

Figure 3 shows the theoretical total energy of a tetragonal structure with space group $I4/mmm$ as a function of tetragonality, i.e., c/a . A set of calculations made for a series of a and c was optimized. The energy was found to be minimum when c/a is unity, i.e., for a cubic structure. The result implies that the tetragonality is induced most likely by the heteroepitaxial strain. The energy increase due to the tetragonal deformation is 2 meV/formula unit. This corresponds to an excess energy of the metastable film of $1.6 \times 10^{-2} h \text{ J m}^{-2}$, where h is the film thickness in nanometres. The interfacial energy between substrate and film should be of the order of 1 J m^{-2} . Assuming that the tetragonality of the film is entirely sustained by the interfacial energy, the critical thickness of the film in the present system is 60 nm. The film thickness in the present study is 50 nm, which is close to the critical thickness. This seems to suggest that a choice of a better substrate may improve the stability of the RS film.

In summary, we have succeeded in the synthesis of a high pressure form of ZnO with a rock-salt structure as a thin film by alloying with 15% of MgO. The presence of the rock-salt structure having tetragonal distortion by $c/a = 1.02$ was unambiguously confirmed by x-ray diffraction and NEXAFS. The film can be formed only when MgO(100) substrate is used.

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