Wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ quaternary systems for Photodiodes in visible spectral range

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Abstract

We investigated the optical bandgap engineering of ZnO based quaternary alloy films of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ for photodiodes in visible spectral range. Quaternary alloy films were successfully synthesized by remote-plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD). The wurtzite alloy system has an optical bandgap energy between 2.16 eV and 3.25 eV, which was controlled by the flow ratio of metalorganic sources. The crystal structure and composition was analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). This revealed that carrier compensation effects by alloying with MgO in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ system decreases carrier concentration. Strong compensation effects were observed in the bandgap range of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ between 3.0 eV to 3.25 eV and the carrier concentration decreased to 10^{15} - 10^{18} cm^{-3} . Schottky diodes of PEDOT: PSS/ $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-y})_y\text{O}$ with optical bandgaps in the visible spectral range were fabricated to confirm the viability of photovoltaic applications. The diodes performed photovoltaic characteristics under a Xe-Hg lamp illumination through Schottky junctions. The photoresponse spectra showed a photosensitivity with cutoff energy of 2.23 eV and peak energy of 2.90 eV at 0 V biasing.

Keywords:

Characterization, Crystal structure, Metalorganic chemical vapor deposition, Alloys, Semiconducting quaternary alloys, Heterojunction semiconductor devices

1. Introduction

Demands for sustainable energy and concern on environmental impact have been increasing the interest to develop various energy consumption, conversion and harvesting devices such as light emitting diodes [1,2], solar cells [3,4], or photo-catalyst devices, including dye-synthesized solar cell and photo electrochemical (PEC) water splitting [5,6]. Various metal oxide materials have been investigated for these applications. Among them, zinc oxide (ZnO) has been used and ZnO-based alloy materials consisting with magnesium (Mg), beryllium (Be), cadmium (Cd), copper (Cu), and indium (In) showing a wurtzite structure are candidates for applications in the ultraviolet to visible light spectral range [7-11], owing to its large exciton binding energy at room temperature and a direct bandgap in wurtzite structure. Ternary $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys increase the bandgap of ZnO and has been shown to provide bandgap tuning in the wurtzite phase to around 4 eV for 33-36% Mg [7, 12-13]. Y. R. Ryu *et al.* proposed that the alternative $\text{Zn}_{1-x}\text{Be}_x\text{O}$ ternary alloy is advantageous compared to $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ as it provides a wide range of bandgap tuning potentially up to that of BeO (10.6 eV) [14]. M. Toporkov *et al.* suggested that alloying with BeO in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, which is the quaternary alloy $\text{Zn}_{1-y}(\text{Be}_x\text{Mg}_{1-x})_y\text{O}$, gives rise to enhanced incorporation of both Be and Mg on Zn sites in the wurtzite lattice and optical bandgap modulation up to 5.1 eV has been achieved [15]. Conversely, the ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ alloy provides bandgap tuning of ZnO to lower values and a bandgap of around 1.8 eV has been demonstrated for 69% Cd [9, 13, 16]. Recently, we succeeded in narrowing the bandgap to 1.6 eV, entering in the near infrared region [17]. It is well known that there is still a lack of p-type ZnO and, moreover, CdO shows heavy n-type conductivity (typical electron concentration is $\sim 10^{20} \text{ cm}^{-3}$) as it used a transparent conductive oxide film [18]. Our previous result of Hall measurement in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films showed n-type conductivity with 10^{19} - 10^{20} cm^{-3} of electron concentration [17,19], therefore further work to reduce the residual electron concentration technique was needed to improve device performance. Y. F. Li *et al.* reported that carrier concentration decreases in n-type $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with increasing Mg content, and as $x > 0.1$, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ grown by plasma-assisted molecular beam epitaxy (p-MBE) begins to show p-type conduction [20]. By using remote plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD), nitrogen doped $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films showed p-type conductivity for $x > 0.08$ with N_2 carrier gas [21]. The mechanism of transformation from n to p type with Mg content was investigated by deep level optical spectroscopy (DLOS) [22,23]. It was revealed that the presence of Mg in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ can result in the formation of acceptor levels, whose

concentrations increase linearly with the Mg content, accounting for the observed decreased in the net electron concentration.

In this study, we investigated the quaternary alloy films of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ to tune the optical bandgap in the visible spectral range by RPE-MOCVD. The alloy films were synthesized by controlling Mg and Cd content. The optical and electrical properties were discussed including the carrier compensation effect of Mg doping. Moreover, photodiodes consisting of Schottky junction using polymer electrode (PEDOT: PSS) were fabricated and characterized.

2. Experimental methods

Wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films were fabricated on *a*-plane (11-20) sapphire substrates by RPE-MOCVD. The substrates were cleaned using acetone and ethanol in an ultrasonic bath, prior to loading into the chamber, the substrates were rinsed with deionized water and dried in N_2 . The reactor chamber was pumped down to 0.05 Torr. The susceptor was preheated at 800 °C, and a radio frequency hydrogen plasma (13.56 MHz, 20 W) for 15 minutes was employed to minimize the substrate surface contamination. After pre-heating, the susceptor was cooled down to the growth temperature of 300 - 450°C. Diethylzinc (DEZn), dimethyl cadmium (DMCd), methylcyclopentadienyl magnesium (MeCp_2Mg), and oxygen gas (mixed with hydrogen plasma) were used as zinc source, cadmium source, magnesium source, and oxidizing agent, respectively. The thickness of the samples was determined by means of stylus depth profile meter (Dektak 3), and typical growth rate was 1 $\mu\text{m/h}$.

The bandgap energy of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ quaternary alloys was determined by analysis of the transmittance spectra in the ultraviolet-visible spectrometry. Structural and optical analysis was performed by means of X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy. PL was performed at room temperature by employing a 325-nm-wavelength cw He-Cd laser with an output power of 3 mW as an excitation source. The chemical composition was analyzed by X-ray photoelectron spectrometry (XPS) in ESCA3400 (SHIMAZU) using Mg $K\alpha$ (1253.6 eV) radiation. The carrier concentration was determined by Hall-effect measurements using the van der Pauw configuration. Schottky diodes using circular structure of 100-300 μm diameters were fabricated in a lateral geometry coplanar to extend ohmic contacts. The metal contacts were processed by standard lift-off photolithography. The extended ohmic contacts were defined with

a Ti (10 nm) / Au (50 nm) thermally annealed at 350 °C for 1 min. The sample surface was treated with hydrogen peroxide (H₂O₂) at 100 °C for 1 min, then spin coated with poly[3, 4-ethylenedioxythiophene]: poly-styrenesulfonate (PEDOT: PSS) aqueous solution. The device structure is illustrated in Fig. 6(a). The current-voltage curve is measured by a digital electrometer (KEYTHLEY 4200) with a Xe-Hg lamp (HAMAMATSU). Photocurrent spectra with front illumination were obtained in the 300-700 nm range by using a linearly polarized beam from a 150 W xenon arc lamp filtered by a monochromator.

3. Results and discussion

Table 1 displays the list of quaternary Zn_{1-y}(Mg_xCd_{1-x})_yO sample properties and the results from the verbal overview. The starting materials of binary ZnO and ternary Zn_{1-x}Mg_xO, Zn_{1-x}Cd_xO are also listed up in the table according to the content value. The content was determined by XPS measurements. The sample number # of typical quaternary Zn_{1-y}(Mg_xCd_{1-x})_yO is used in the following discussion. The optical bandgap was defined as an optical absorption edge determined by the optical absorption from the transmittance spectra, where the relationship between the absorption coefficient (α) and the optical bandgap of semiconductor (opt-Eg) is described by the following equation [24]:

$$\alpha h\nu = A(h\nu - E_g^{opt})^x \quad (1)$$

where A is constant, $h\nu$ is the energy of incident photons, and x is a parameter and its value is 0.5 for a direct semiconductor. The optical bandgap was obtained by the intercept of the linear region in plotting $(\alpha h\nu)^2$ versus $h\nu$. The ZnO-based oxide semiconductors tend to n-type conductivity, the dopant atoms are then ionized and the associated electrons occupy the bottom of the conduction band in the form of an electron gas. When the Mott critical density of ZnO is $7 \times 10^{19} \text{ cm}^{-3}$ [25,26], the optical bandgap can be larger since the lowest states in the conduction band are blocked. This is the well-known Burstein-Moss (BM) effect. In this study, we define the bandgap is the optical bandgap the energy estimated from the absorption edge in the transmittance spectra and the BM shift of the optical bandgap for the heavily doped samples. Meanwhile, the monotonic redshift of the near-band-gap emission detected by PL measurements has also been observed with increasing free-carrier concentration, which is attributed to the nonparabolic nature of conduction band and bandgap renormalization (BGR) effects [27]. Where also discuss photoluminescence and carrier concentration section.

Figure 1(a) shows the transmittance spectra of a series of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ quaternary alloy films in the visible spectral range, together with that of ZnO and the starting materials $\text{Zn}_{0.83}\text{Mg}_{0.17}\text{O}$ and $\text{Zn}_{0.46}\text{Cd}_{0.54}\text{O}$ as a reference. The $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films were designed through the systematic control of a molecular molar ratio of metalorganic source based on the growth conditions of the ternary alloy systems. The dashed lines show the square absorption coefficient in the range of $1 \times 10^{10} \text{ cm}^{-2}$, which are used to determine the optical bandgap (opt-Eg). ZnO has an opt-Eg of 3.3 eV and the $\text{Zn}_{0.83}\text{Mg}_{0.17}\text{O}$ has an opt-Eg of 3.55 eV at room temperature. The incorporation of Cd in the $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ alloy is accompanied by a systematic low-energy shift of the optical bandgap extending down to the red spectral range. The samples appear homogeneous with a color changing from transparent to red, and show a sharp transition near the absorption edge. The optical bandgaps of three representative alloy compositions are 3.10 eV for the blue, 2.77 eV for the blue-green, and 2.16 eV for the red, respectively. The optical bandgap energy of visible spectral range $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ depended on the Cd content, which results in a redshift of the band-edge emission peak. Figure 1(b) shows the respective photoluminescence spectra. All of the photoluminescence spectra exhibit intense near-band-edge transitions are attributed to carrier localization and Stokes' shift and extremely weak defect related deep-level emission under the excitation of 325 nm He-Cd laser at room temperature. In principal n-type ZnO system, an absorptive optical transition occurs from the valence band to conduction band or the Fermi level, while an emissive transition occurs from an impurity-donor band to the valence band. This is due to the occurrence of a Stokes' shift, i.e., the luminescence peak is red shifted from the absorption threshold. The broadening in the PL spectra with increase of both of Cd and Mg content is shown, which is a similar tendency to that of the carrier concentration. The dominant luminescence transition is thought to be due to such a donor-to-free-hole recombination, because the Stokes' shifts exceed a sum of the donor and acceptor ionization energies in samples at the highest doping levels.

Figure 2(a) shows typical XRD 2θ scans taken from representative $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films including ZnO. The peak position of the Bragg reflection in the ZnO film on *a*-plane sapphire substrate coincides with that of a characteristic (0002) reflection in wurtzite ZnO. For the samples doped with Cd and Mg, there is a shift toward lower Bragg angles. This is expected from a substitution of Zn atom (0.60 Å) by Cd atom (0.78 Å) and Mg atom (0.57 Å) on equivalent crystallographic positions in the wurtzite lattice. No distinct peaks related to reflections from *rs*-CdO were observed, indicating that they are single-phase wurtzite materials. The

energy-shift of the optical bandgap with alloy content was in good agreement with the previous results of bandgap bowing [13]. However, the alloy broadening of the PL energy shift was remarkably large for $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ system, as shown in Fig. 2(b). In general, alloy fluctuations cause alloy broadening in the PL spectra. The Stokes' shift value of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ two times larger than in the ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ system even the carrier concentration was suppressed. To explain the large Stokes' shift, we speculated a mechanism; the nonparabolicity of the conduction band in the host wurtzite ZnO crystal enhanced by alloying with both rock-salt MgO and CdO. The fundamental bandgap of ZnCdO is blue shifted with substitution of Mg in Zn site, however, the relative Cd composition ratio (Zn:Cd) is increased. The recombination of free-electron-to-valence band may transit at the lower energy, the Stokes' shift occurs in red shifted. Figure 2(c) shows a relationship between the optical bandgap and the wurtzite *c*-axis length of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ alloy systems. The as-grown ZnO film has a bandgap of 3.3 eV and a *c*-axis length of 0.5206 nm. The starting materials of $\text{Zn}_{0.83}\text{Mg}_{0.17}\text{O}$ and $\text{Zn}_{0.46}\text{Cd}_{0.54}\text{O}$ show 3.55 eV, 0.518 nm and 1.73 eV, 0.540 nm, respectively. It is found that there is a correlation between the optical bandgap and the *c*-axis length even in the quaternary alloy system by means of a Vegard's law, as in the case of ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ systems [13].

Figure 3(a) shows plots of the optical bandgap of wurtzite phase $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ as a relationship between the source of Mg and Cd molar flow ratio during film growth. The Zn source was constant value of 4 $\mu\text{mol/min}$ and the growth temperature at 350 to 400°C. The lozenge solid in red shows wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ in single phase and in gray shows a polycrystalline phase in films. The composition in $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ was systematically designed by the ratio of metalorganic sources and the growth temperature. The growth parameters were calculated based on the Fig. 4. We present a model which can explain semi-quantitatively an incorporation ratio of Mg/Cd in $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ as a growth temperature. The optimum growth temperature of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and ZnO to obtain wurtzite phase is 400 °C and more, typically, around 600 °C. In contrast to $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, wurtzite phase of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ requires a low temperature in the 300-500 °C range. Indeed, we confirmed Cd evaporation effect on $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ by thermal annealing up to 550 °C in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ (300 °C) [28]. The sample #1 (opt-Eg of 3.26 eV) was grown with Mg:1.51 $\mu\text{mol/min}$, Cd:1.1 $\mu\text{mol/min}$ at 400°C. When we increase the Mg and the Cd flow, for example, sample #3 shows red shift of bandgap as 2.98 eV (Mg:1.68 $\mu\text{mol/min}$, Cd:1.86 $\mu\text{mol/min}$). At the same Cd flowrate (Cd:1.86 $\mu\text{mol/min}$), we can see the same bandgap of 2.25 eV with different Mg flowrate (above point is 2.7 $\mu\text{mol/min}$, lower point is 1.26

$\mu\text{mol/min}$). They indicate that the Mg incorporation was limited at 400°C , resulted in the same bandgap (same Cd composition in the films). Moreover, the Cd incorporation limit was on the growth temperature. When we decrease the Cd flowrate from Cd:1.86 $\mu\text{mol/min}$ (sample #3) to Cd:1.26 $\mu\text{mol/min}$, the opt-Eg showed 2.83 eV, where decreased the energy 0.15 eV from that of sample #3. When we lowered the growth temperature to 350°C , the sample #5 showed the opt-Eg of 2.37 eV and the Cd well incorporated into the film as a result of sample #6 (2.16 eV).

Figure 3(b) shows a relationship between the optical bandgap and carrier concentration. The typical experimental results of quaternary $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})\text{O}$ films were plotted including ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films. The ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ showed heavily n-type conduction and the carrier concentration were in the range of $10^{19} - 10^{20} \text{ cm}^{-3}$. This is possibly due to the narrowing optical bandgap with large amount of electron donor levels. In previous studies, we reported that there are electron trap levels in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, and these trap concentration increase with the decrease in the net electron concentration with increasing Mg content. Particularly, and due to its large trap concentration, the $E_v+280 \text{ meV}$ level seems to be the dominant acceptor level that is responsible for the strong carrier compensation effect observed at high Mg contents [22]. The carrier concentration of ternary $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ decreased from $2.7 \times 10^{17} \text{ cm}^{-3}$ to $1.3 \times 10^{16} \text{ cm}^{-3}$ monotonically with increasing of PL energy [21-23]. The carrier compensation effect was remarkably observed in the quaternary alloy of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$. Yang *et al.* pointed out that a $\text{Zn}_x\text{Mg}_{1-x}\text{O}$ alloy is subjected to the wurtzite-rocksalt phase transition, while a $\text{Zn}_{1-x}\text{Be}_x\text{O}$ alloy is not, and they proposed substituting the appropriate amount of Zn for Be site in $\text{Zn}_x\text{Mg}_{1-x}\text{O}$ [29]. It is considered that the big difference of ionic radii between Zn^{2+} (0.6 Å) and Be^{2+} (0.27 Å) may influence the thermodynamic stability of wurtzite crystal structure. D.Y. Yong *et al.* successfully demonstrated that as the content of Be increases, the maximum content of Mg in wurtzite $\text{Be}_x\text{Mg}_y\text{Zn}_{1-x-y}\text{O}$ alloy increases accordingly [30]. In the case of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ system, the ionic radii of Cd^{2+} (0.78 Å) is much larger than that of Zn^{2+} (0.6 Å) and Mg^{2+} (0.57 Å), but the existence of Mg ion among the alloy components possibly enhances the substitution of Cd ion for Zn.

Figure 4 shows the experimental data of the optical bandgap energy counter for quaternary alloys. The starting materials are w-ZnO, rs-MgO, and rs-CdO, which have a direct energy gap of 3.3 eV, an in-direct gap of 7.8 eV, and 2.2 eV including a direct transition of 0.75 eV [31], respectively. The maximum Mg content in wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ was reported by A. Ohtomo *et al.* as $x=0.3$ in 3.9 eV [7]. L. Su *et al.* reported that the

phase transition point is 0.33 by means of the formation energies of wurtzite and rock-salt $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ as linear functions of Mg concentration [32]. The maximum Cd concentration in wurtzite $\text{Zn}_{1-y}\text{Cd}_y\text{O}$ in this work was $y = 0.7$ in 1.6 eV [17]. The triangle region where the structural element of ZnO, the maximum Mg content at $x = 0.3$, and the maximum Cd content at $y = 0.7$ show the compositions for the quaternary alloy is expected to be wurtzite structure, and the white regions show a rocksalt structure with an indirect transition. The dashed line is an expected boundary for mixed phase. The optical bandgap energy of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and $\text{Zn}_{1-y}\text{Cd}_y\text{O}$ were calculated using the previous reported equation as a function of alloy content in the host ZnO [13, 33]. It is noted that Vegard's law holds well for the lattice parameter as shown in Fig.3(b). Therefore, it can be considered that Mg and Cd atoms exist at the host lattice of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ by substituting the Zn site. We can assume the optical bandgap energy as linear relationship between $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and $\text{Zn}_{1-y}\text{Cd}_y\text{O}$ for $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$. The dot lines are calculated value of the optical bandgap in quaternary alloys without considering the bowing parameter. The experimental results plotted with the counter curve of an optical bandgap energy are shown as circles. The red-solid circles agreed with the calculation the representative content $0 \leq xy (\text{Mg}) \leq 0.05$ and $0 \leq (1-x)y (\text{Cd}) \leq 0.1$. For example, the sample #2 showed the optical bandgap of 3.1 eV (the calculate value was 3.1 eV) with Zn $(1-y) = 0.91$, Mg $(x) = 0.7$, Cd $(1-x) = 0.3$, $y = 0.09$, respectively, as shown in Table 1. However, when Mg+Cd content $(y) > \sim 0.12$, the optical bandgap energy showed lower bandgap energy of 0.5~0.7 eV compared with the calculation corresponding to those compositions. Figure 5 shows schematic band structure with parabolic conduction and valence bands in intrinsic semiconductor separated by E_{g0} (a), with heavy doping and the optical bandgap widened by BM shift (b), and a perturbed band structure and ensuing optical bandgap (c). The shaded areas denote occupied states. The optical bandgap is defined as the minimum energy needed to excite an electron from the valence band to the conduction band. In the undoped semiconductor, the optical bandgap equals the energy separation E_{g0} between the band edges as shown in Fig.5(a). In a heavily doped semiconductor, the donor electrons occupy states at the bottom of the conduction band, the blocking of the low-energy transitions is the Burstein-Moss (BM) effect as shown in Fig.5(b). In a medium doped $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ ($< 10^{20} \text{ cm}^{-3}$), we speculate the case of isotopic and non-parabolic bands due to many body effect [33,34] as shown in Fig.5(c). Therefore, the calculation of the optical bandgap in $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ in Fig.4 should take account the BM shift, and the fundamental optical bandgap (E_{g0}) will be small at least ~ 0.5 eV.

To realize a Schottky barrier in the ZnO-based films, there are obstacles such as a high residual electron density, surface traps, oxidation of Schottky metals, etc. Among them, a reduction of the residual electron concentration is considerably effective for producing a stable Schottky barrier. The ideal barrier height Φ_{B0} is given by

$$\Phi_{B0} = \Phi_M - \chi \quad (2)$$

where Φ_M is the work function of the metal and χ is the electron affinity of the semiconductor, defined as the potential difference between the bottom of the conduction band and the vacuum level at the semiconductor surface. However, the actual barrier height Φ_B is less than Φ_{B0} due to image force barrier lowering and other factors as those described above. The barrier height is given by

$$\Phi_B = V_{bi} + V_o \quad (3)$$

where V_{bi} is the built-in potential and V_o is the potential of the semiconductor Fermi level with respect to the conduction band ($E_C - E_F$), expressed as

$$V_o = k_B T \ln(N_C/N_D) \quad (4)$$

where N_C is the effective density of states in the conduction band and, N_D is the donor density. N_C of ZnO is reported as $4 \times 10^{18} \text{ cm}^{-3}$ and the χ of ZnO is 4.1-4.4 eV [35,36]. When we select a large work function metal as the Schottky contact such as a conducting polymer of PEDOT: PSS (5.0 eV), the ideal Schottky barrier is evaluated to be 0.7-0.9 eV. Taking into account for the image force lowering, a low carrier concentration under N_C is preferable to obtain a good Schottky barrier. Figure 6(a) shows a cross sectional view of PEDOT: PSS/Zn_{1-y}(Mg_xCd_{1-x})_yO Schottky diode and a top view optical microscope picture. Figure 6(b) shows the typical dark and illuminated current-voltage (J - V) characteristics of PEDOT: PSS Schottky diodes on Zn_{1-y}(Mg_xCd_{1-x})_yO (sample #3) with optical bandgap of 2.98 eV and n of $3.6 \times 10^{18} \text{ cm}^{-3}$, respectively. The dark J - V characteristics showed rectifying behavior with absolute current densities at a forward bias of 3V and at a reverse bias of -3 V, $1.3 \times 10^{-4} \text{ A/cm}^2$ and $3.9 \times 10^{-8} \text{ A/cm}^2$, respectively. The rectification ratio was as high as 10^4 at bias voltage of $\pm 3 \text{ V}$, indicating the formation of a good Schottky contact on the Zn_{0.88}(Mg_{0.2}Cd_{0.8})_{0.12}O surface. With irradiation of Xe-Hg lamp, the reverse bias current increases by 25 times at -3 V, suggesting photo-sensitivity for this Schottky junction. T. Ikenoue et al. [36] also reported the highly rectifying performance for PEDOT: PSS/Zn_{1-x}Mg_xO Schottky diode with a current rectification ratio of 10^4 at $\pm 2 \text{ V}$ and leakage currents as low as 100 nA up to -5 V. The short-circuit current density (J_{sc}) was $0.03 \mu\text{A/cm}^2$

and the open-circuit voltage (V_{oc}) was 129 mV. The $\text{Zn}_{0.88}(\text{Mg}_{0.2}\text{Cd}_{0.8})_{0.12}\text{O}$ of 2.98 eV bandgap might sensitively detect visible light. Note that the V_{oc} exhibited low values (around 129 mV), which was much lower than photo voltage observed in PEDOT: PSS Schottky contacts on ZnO single crystal ($V_{oc} = 360$ mV) [37], because of the difference of the built-in potential at the Schottky junction owing to the higher carrier concentration of $\text{Zn}_{0.88}(\text{Mg}_{0.2}\text{Cd}_{0.8})_{0.12}\text{O}$ film. Moreover, very recently, R. Karsthof et al. reported excellent PV performance NiO/ZnO through p-n junctions ($V_{oc}=0.51$ V) [4]. Figure 6(c) shows the responsivity spectra recorded at 0 V and -1 V, respectively, and the room temperature PL spectrum and transmittance spectra. The photoresponse properties were shown in Table 2. When the 0V biasing is applied on the sample #3, the responsivity started to rise at around 2.23 eV (cutoff energy: λ_{co}), where the transmittance spectra were started to quench, and became saturated at around 3.3 eV (λ_{peak}) over bandgap energy, where was the absorption edge in the transmittance spectra. When we applied -1 V on the diode, the on/off ratio ($I(\lambda_{peak})/I(\lambda_{co})$) was declined to 1 order of magnitude due to the leakage current of the diode, but it clearly appeared the photoresponse at the $\lambda_{co}-\lambda_{peak}$ of around 2.14-3.19 eV. The red-shift of λ_{peak} and λ_{co} with biasing is due to increase of the depletion layer depth and penetration volume, resulting in an increase of the surface recombination and increase of the leakage current. The responsivity of the Schottky diode is $\sim 2.5 \times 10^{-3}$ A/W at -1.0 V biasing and $\sim 5.3 \times 10^{-5}$ A/W at 0 V biasing, respectively. The higher responsivity (3.2×10^1 A/W at -1.5 V) for $\text{Au}/\text{Zn}_{1-y}\text{Mg}_y\text{O}$ and the close value (3.3×10^{-5} A/W at 0 V) were obtained [38]. The photoresponse at 0 V is regarded as a photodiode mode, and the penetration depth of photon, where is the depletion layer, is depended on the Schottky barrier height. The photoresponse with applying voltage is regarded as an avalanche photodiode mode, the photogenerated current and the internal gain are associated with the Schottky barrier height. The carrier concentration of #3 was $3.6 \times 10^{18} \text{ cm}^{-3}$, that of the $\text{Zn}_{1-y}\text{Mg}_y\text{O}$ was $1.6 \times 10^{16} \text{ cm}^{-3}$. The depth of the depletion layer is roughly estimated to few nanometer for #3, and few micrometers for the $\text{Zn}_{1-y}\text{Mg}_y\text{O}$. However, the Schottky interface on ionic materials associated with dipole makes a reduction of photogenerated voltage (i.e. open circuit voltage in a photovoltaic) and induces high persistent photoconductivity (i.e. slow transient of photogenerated states) [39]. It is not clear yet, the $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ system with the middle range of carrier concentration as $\sim 10^{18} \text{ cm}^{-3}$ can decrease the dipole effect resulted in obtaining the $V_{oc} = 129 \text{ meV}$.

4. Conclusions

Quaternary alloy films of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ were successfully synthesized by RPE-MOCVD technique. The optical bandgap was tuned in the visible spectral range and the property of the optical bandgap were discussed. The wurtzite alloy system has an optical bandgap between 2.16 eV and 3.25 eV, and a carrier concentration between 10^{15} - 10^{18} cm^{-3} . A preferable advantage as alloying with MgO in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ can explain well the strong carrier compensation effect observed with existing Mg contents, and is likely at the origin of the amenability to p-type doping in $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$. Schottky diodes of PEDOT: PSS/ $\text{Zn}_{0.88}(\text{Mg}_{0.2}\text{Cd}_{0.8})_{0.12}\text{O}$ with visible spectral range bandgaps performed a rectifying behavior. We demonstrated photodiodes using the $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ alloy films.

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Figure captions

Table 1. Characteristics summary of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ alloy systems and PV performance

Fig. 1. (a) The optical transmittance spectra of a series of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ together with ZnO , $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and the plots of the square absorption coefficient as a function of photon energy. The optical bandgap was determined in the linear fit at the range of 0 to $1 \times 10^{10} \text{ cm}^{-2}$.

(b) The photoluminescence spectra of typical series of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films including ZnO measured at room temperature. The transmittance and the square absorption coefficient were also set in the figure as a reference.

Fig. 2. (a) The XRD patterns of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films on *a*-plane sapphire substrate including ZnO film for a reference.

(b) and (c) The room temperature PL energy and the optical bandgap of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ films as a function of the *c*-axis length, which were calculated from the (0002) diffraction peak in XRD patterns. ZnO and the starting $\text{Zn}_{0.83}\text{Mg}_{0.17}\text{O}$ and $\text{Zn}_{0.46}\text{Cd}_{0.54}\text{O}$ were also shown in this plot. The data of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ which are previously reported value are also shown in this figure.

Fig. 3. (a) The PL energy of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ as a relationship in experimental molar supply between Cd and Mg.

(b) The carrier concentration of wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ including $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ as a function of optical bandgap energy.

Fig. 4. Experimental data of the optical bandgap energy counter for quaternary alloys. The optical energy bandgaps are in eV. The calculated optical bandgap based on ternary system were also indicated.

Fig. 5. Schematic band structure with parabolic conduction and valence bands in intrinsic semiconductor separated by E_{g0} (a), with heavy doping and the optical bandgap is widened by BM shift (b), and a perturbed

band structure and ensuing optical bandgap (c). The shaded areas denote occupied states. Here, k is wave vector and the $\hbar\omega$ is energy. The Fermi wave vector k_F is also indicated.

Fig. 6. (a) A cross sectional view of PEDOT: PSS/Zn_{1-y}(Mg_xCd_{1-x})_yO Schottky diode and top view of optical microscope picture. (b) The typical dark and lamp illuminated current-voltage (J - V) characteristics of PEDOT: PSS Schottky diodes on sample #3 with optical bandgap of 2.98 eV and carrier concentration (n) of $3.6 \times 10^{18} \text{ cm}^{-3}$, respectively. (c) The responsivity of the Schottky diodes of PEDOT: PSS/Zn_{0.88}(Mg_{0.2}Cd_{0.8})_{0.12}O (sample #3) with the room temperature PL spectrum and transmittance spectra of sample #3.

Table 2. Photoresponse properties of PEDOT: PSS/Zn_{1-y}(Mg_xCd_{1-x})_yO

FIG 1A

FIG 1B

FIG 2A

FIG 2BC

FIG 3A

FIG 3B

FIG 4

FIG 5

FIG 6A

FIG 6B

FIG 6C

Table 1. Characteristics summary of $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ alloy systems and PV performance

Materials	System	Growth Temperature (°C)	XPS contents				Carrier concentration (cm^{-3})	Opt-Eg (eV)	PL (eV)	PV		comment
			Zn	Mg	Cd					J_{sc}	V_{oc}	
			1-y	x	1-x	y				($\mu\text{A}/\text{cm}^2$)	(mV)	
$\text{Zn}_{0.83}\text{Mg}_{0.17}\text{O}$	ternary	400	0.83	1.0	0	0.17	1.3×10^{16}	3.55	3.44	0.9	50	rectifying [18-20]
ZnO	binary	400	1.0	0	0	0	2.7×10^{17}	3.30	3.28	12.3	170	rectifying
#1 $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$	quaternary	400	*	*	*	*	5.8×10^{17}	3.26	3.0	11.3	60	rectifying
#2	quaternary	400	0.91	0.7	0.3	0.09	2.6×10^{16}	3.10	2.91	(**)	(**)	(not processed)
#3	quaternary	400	0.88	0.2	0.8	0.12	3.6×10^{18}	2.98	2.60	0.03	129	rectifying
#4	quaternary	400	0.89	0.6	0.4	0.11	7.1×10^{19}	2.77	2.67	-	-	
#5	quaternary	350	0.87	0.4	0.6	0.13	8.4×10^{19}	2.82	2.37	-	-	
#6	quaternary	350	0.82	0.16	0.83	0.18	8.5×10^{19}	2.16	2.02	-	-	
$\text{Zn}_{0.46}\text{Cd}_{0.54}\text{O}$	ternary	350	0.46	0	1.0	0.54	1.0×10^{20}	1.73	1.68	-	-	

*: XPS, Not available **: Not available

Table 2. Photoresponse properties of PEDOT:PSS/ $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$

Schottky /	responsivity		$(I_{\text{peak}})/(I_{\text{cutoff}})$		$\lambda_{\text{cutoff}} - \lambda_{\text{peak}}$		PL	Opt-Eg	XPS contents				n
	(A/W)		(-)		(eV)				Zn	Mg	Cd	y	
	@ -1 V	0 V	@ -1 V	0 V	@ -1 V	0 V			(eV)	(eV)	1-y		x
#3	2.5×10^{-3}	5.3×10^{-5}	16	370	2.14-3.19	2.23-3.30	2.60	2.98	0.88	0.2	0.8	0.12	3.6×10^{18}
Au / Zn _{1-y} Mg _y O ^[29]	$3.2 \times 10^{1*}$	(3.3×10^{-5})	1500*	(33)	3.41-3.66*	(3.41-3.60)	3.44	3.54	0.82	1.0	0	0.18	1.3×10^{16}

* : @-1.5V