

Title	Effect of microwave irradiation on the electronic structure of ZnO
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Citation	Journal of Physics and Chemistry of Solids (2015), 83: 47-51
Issue Date	2015-03-14
URL	http://hdl.handle.net/2433/198552
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Type	Journal Article
Textversion	author

1 Effect of microwave irradiation on the electronic structure of ZnO

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14 Modifying the electronic structure may allow a bulk material to efficiently absorb
15 radiation as well as excite and emit atomic plasma. The interaction between microwaves
16 and metal oxides is investigated by analyzing the electronic structure of ZnO with and
17 without microwave (MW) irradiation using absorption, photoluminescence (PL), and PL
18 excitation (PLE) spectroscopies and utilizing an ultraviolet synchrotron light source.
19 MW irradiation lowers the energy of the absorption edge of ZnO producing defects.
20 Additionally, MW irradiation causes a resonantly enhanced change in the intensity and
21 peak shift of the PL band. These phenomena indicate that the defects generated by MW
22 irradiation change the electronic structure of ZnO and the electron transition process.

23
24
25 **KEYWORDS:** electronic structure; optical properties; semiconductors; inorganic
26 compounds; oxides

27

1 **1. Introduction**

2 Microwave (MW) heating is an advanced method for materials processing due to its
3 unique advantages such as rapid and selective heating compared to conventional
4 methods [1]. To date, several approaches have been implemented. For example, MW
5 heating in the liquid phase has enhanced the catalytic activity of ZnO and MgO [2,3]. It
6 also can create ZnO architectures such as ZnO nanorods, wire-like, or flower-like
7 structures [4,5]. Additionally, MW sintering has been reported to improve the electronic
8 property of ZnO as a varistor for semiconductor application [6-8].

9 Sonobe et al. reported that the surface modification of TiO₂ for enhancement of
10 catalytic activity and the direct reduction without a reducing agent of TiO₂ were
11 available by MW treatment [9,10]. Similarly, the enhancement of the photocatalytic
12 activity of PbMoO₄ by MW irradiation has been reported[11]. Thus, MW technology
13 has been used in advanced materials processing to improve the properties of functional
14 materials.

15 MW heating of ZnO enhances the photocatalytic activity, synthesis of ZnO
16 architectures, improvement of the capability as a varistor or thin film fabrication and so
17 on [2,6-8,12,13]. In addition, the interaction between microwaves and ZnO has been
18 investigated [14]. It was also confirmed that the MW irradiation did not induce the
19 change of the crystallinity of ZnO [13]. In a previous study [14], a phenomenological
20 model was constructed without exploring the detailed electronic structure in the
21 bandgap which was created by MW irradiation. A phenomenological model is useful to
22 design MW-induced Zn/O atomic plasma excitations and emissions, or
23 oxidation/reduction of bulk ZnO. The change in the physical properties such as the
24 electronic structure by MW heating should be indispensable to elucidate this
25 mechanism.

26 Moreover, the electronic structure is a significant parameter with respect to the
27 capability of a functional material such as a photocatalyst or an electronic device.
28 Therefore, the effect of MW irradiation on the electronic structure has been also
29 investigated [1,5,15]. Previous research by our group [13] includes investigation of the
30 changes in both the absorption and PL spectra with MW irradiation. The observed
31 emergence of bandgap absorption and the change in the PL band suggest that
32 MW-induced defects are created. However, the correspondence between the enhanced
33 PL band and the bandgap absorption was not confirmed. Therefore, details of the
34 electronic structures with MW irradiation such as the change in the electron transition
35 process have yet to be investigated.

36 To apply MW heating technology for material processing, the objective of this research

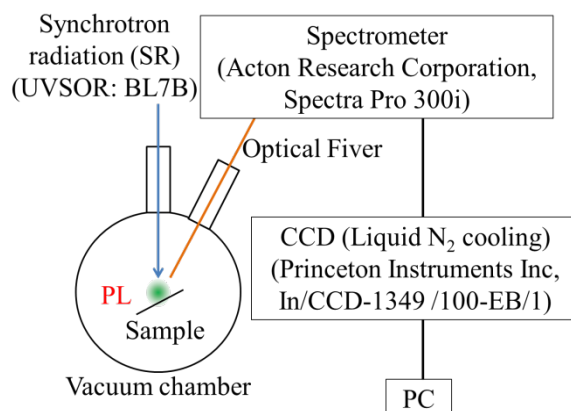
1 is to clarify the effect of MW irradiation on the electronic structural change of ZnO.

2 This study employs absorption, photoluminescence (PL), and PL excitation (PLE)
 3 spectroscopies to analyze the electronic structure of ZnO with MW irradiation. The
 4 absorption spectra provide details about the energy shift of the absorption edge of ZnO
 5 through MW irradiation, while the PL spectra provide information not only about the
 6 electronic structure of the material but also about the defects or impurities. In addition,
 7 the PLE spectra help to understand the difference between the excitation mechanisms
 8 with and without MW irradiation as well as provide insight on the electronic structure
 9 and the electron transition process.

11 2. Material and Methods

12 Commercially available ZnO powder (1 g) (Wako Pure Chemical Industry, - 5 μ m
 13 99.9%) was pressed into a rectangular pellet ($27.0 \times 6.7 \times 1.5$ mm³) and sintered in air
 14 by a furnace at 873 K for 2 h before MW irradiation. Then the sample exposed to
 15 500-W MW irradiation for 10 min using reactor under vacuum conditions with a
 16 vacuum pressure of about 1 Pa and a MW frequency of 2.45 GHz (wavelength : 124
 17 mm). Details about MW irradiation are reported elsewhere [13].

18 The absorption spectra were acquired with a UV-VIS-NIR spectrometer (JASCO,
 19 V-670). BL7B beamline in UVSOR [16] was used as the light source for PL and PLE
 20 spectroscopies. Figure 1 depicts the experimental setup for PL and PLE spectroscopies.
 21 The photon energy of the excitation light was varied between 2.92 eV (425 nm) and
 22 3.54 eV (350 nm). A spectrometer (Acton Research Corporation, Spectra Pro-300i) and
 23 a CCD cooled by liquid nitrogen (Princeton Instruments Inc, In/CCD-1340/100-EB/1)
 24 were used for PL detection. The exposure time, measurement temperature, and energy
 25 resolution of the excitation light were 10 s, room temperature, and 0.02 eV (FWHM)
 26 respectively.



27
 28 Fig. 1. Schematic of the setup for PL and PLE spectroscopies

1 In addition, PL spectroscopy with a He-Cd laser (wavelength: 325 nm (3.81 eV),
 2 power: 10 mW, beam diameter: 1.0 mm: Kimmon IK5451R-E) was conducted at low
 3 temperature (14 K) to investigate the band structure. The emission was observed by a
 4 spectrometer (Zolix, Omni- λ 300) with a CCD array (INTEVAC Mosir 350) and an
 5 exposure time of 1 s.

6 All data shown in this paper was corrected from single sample. To check the
 7 sample-to-sample variation of the phenomenon, several samples were prepared and it
 8 was confirmed that the same phenomenon was observed in samples prepared in same
 9 condition.

11 3. Results and Discussion

12 3.1 Absorption spectra

13 Absorption spectroscopy was conducted with an emphasis on the absorption edge.
 14 Figure 2 shows the absorption coefficient spectra. These spectra were converted from
 15 the diffuse reflection spectra using Kubelka-Munk formula [9, 17], which is
 16 expressed by Eq. (1) as

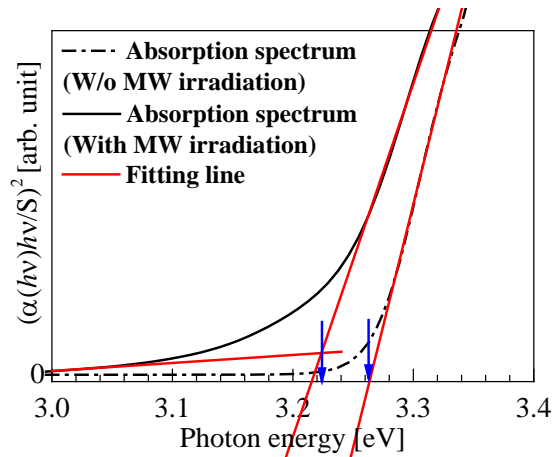
$$\alpha / S = (1 - R)^2 / 2R. \quad (1)$$

17 Here, α is the absorption coefficient, S is the scattering coefficient, and R is the diffuse
 18 reflectance. S is assumed to be constant, which is usually reasonable around the
 19 absorption edge [9].

20 The energy of absorption edge of ZnO with or without MW irradiation were calculated
 21 using Eq. (2) as [18, 19]

$$(h\nu\alpha)^2 = C(h\nu - E_g). \quad (2)$$

22 Here, $h\nu$ is the photon energy (h is Planck's constant and ν is the frequency of light), C
 23 is a constant, and E_g is the energy of the absorption edge. The blue arrows in Fig. 2
 24 indicate the energy of the absorption edge determined from the absorption spectra. The
 25 energies of the absorption edges of ZnO without and with MW irradiation are around
 26 3.26 eV and 3.22 eV, respectively. The absorption edge energy of the sample with MW
 27 irradiation (3.22 eV) is lower than that without MW irradiation (3.26 eV) (Phenomenon
 28 1), suggesting that MW irradiation reduces the bandgap energy or creates new electronic
 29 states below the conduction band.



1
2 Fig. 2 $(h\nu\alpha / S)^2$ as a function of photon energy for the absorption edge of ZnO with
3 and without MW irradiation. Red lines are visual guides for $h\nu\alpha \propto (h\nu - E')^{1/2}$ and to
4 evaluate the absorption threshold ($E' = E_g$ for energy of the absorption edge)

5 6 3.2 PL and PLE spectra at room temperature

7 To confirm the defect-level energy, PL spectroscopies were investigated as functions of
8 excitation energy. Figures 3 and 4 show the PL spectra for several excitation energies.
9 The broad peaks between 2.70 eV and 3.50 eV are the excitation light and the sharp
10 peaks between 1.50 eV and 1.80 eV are inherently generated by the second order
11 diffraction of the excitation light on the grating used to measure the PL spectra. The
12 case without MW irradiation contains broad peak at 2.20 eV and a band-edge emission
13 at 3.20–3.30 eV (Fig. 4). To confirm that observed broad peaks are PL from the ZnO, a
14 PL measurement with another material was conducted. The measurement was
15 conducted on commercially available TiO_2 powder (Furuuchi Chemical Corporation,
16 TIC-72208B, -300M, purity:99.99%) pressed into a rectangular pellet ($27.0 \times 6.7 \times 1.5$
17 mm^3) of the same form with ZnO pellet and sintered in air by a furnace at 1273 K for 6
18 h. The crystal structure of the prepared TiO_2 pellet was rutile [20]. The TiO_2 pellet was
19 irradiated the photon of 350 nm with the exposure time of 10 s. The prepared TiO_2
20 sample is white color and barely shows the absorption in visible region [20]. As shown
21 in Fig. 3 (a), no peaks were observed in the case of TiO_2 pellet. If the origin of the
22 observed broad peak is the measurement system such as the stray light of the excitation
23 light, the similar peak with higher intensity should be observed in the case of TiO_2
24 because the collected photon in spectrometer in the case of TiO_2 is larger than that of the
25 case of ZnO as shown in Fig. 3 (b). These facts show that the observed broad peak is the
26 PL from ZnO. As the result, the intensity of the broad peak at 2.20 eV is nearly constant
27 regardless of the excitation energy (Phenomenon 2). Thus, the transition process of ZnO

1 is independent of the excitation energy without MW irradiation.

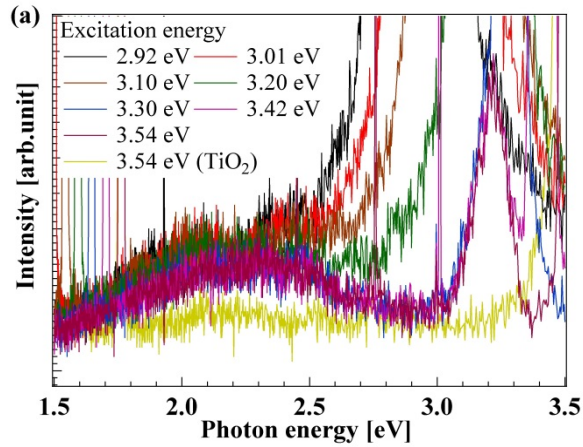
2 However, in the case of the MW irradiation, the emission intensity of the broad peak
3 around 2.40 eV strongly depends on the excitation energy, and the highest emission
4 intensity occurs with an excitation energy of 3.20 eV (Fig. 4). This phenomenon implies
5 that the electron transition process was changed when the excitation energy was
6 changed.

7 PLE spectroscopy was conducted to understand the detailed electronic structure and
8 the electron transition process in the sample with MW irradiation. The upper panel and
9 right panel in Fig. 5 show the horizontal cross-section in which the excitation photons
10 emerge at 3.23 eV and 3.35 eV, and the vertical cross-section whose photon energies in
11 the PL are 2.31 eV and 2.20 eV in the 2D graph, respectively. The small peak shift in
12 the central energy in the broad PL peak from 2.31 eV (vertical red line) to 2.20 eV
13 (vertical black line) occurs when the excitation energy is changed from 3.23 eV to 3.35
14 eV. The broad peak (around 2.31 eV) has the highest PL when the excitation energy is
15 3.23 eV. These results show that the emission intensity of the broad peak depends on the
16 excitation energy and that the maximum occurs at 3.23 eV (Phenomenon 3). The broad
17 peak shifts from 2.31 eV to 2.20 eV as the excitation energy is elevated from 3.23 eV to
18 3.35 eV (Phenomenon 4).

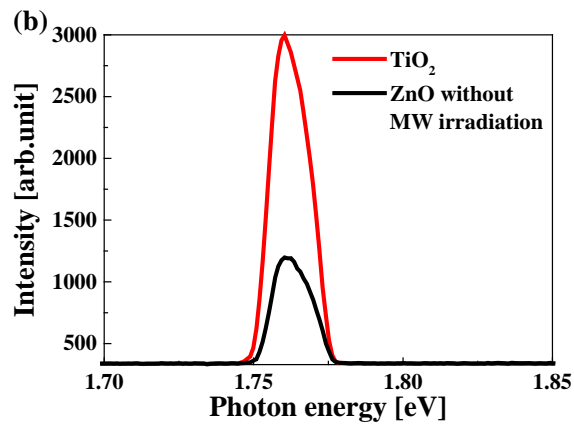
19 The peak at 2.20–2.40 eV in ZnO is attributed to point defects such as oxygen
20 vacancies, zinc vacancies, zinc interstitials, oxygen interstitials, and oxygen-antisites
21 [21- 27]. The electron transition process changes as the excitation energy is swept and
22 has a maximum of approximately 2.31 eV when the excitation energy is 3.23 eV.
23 Therefore, the electron is trapped strongly at this energy level (3.23 eV). Because the
24 excitation energy resolution in the PLE is sufficiently high (around 0.02 eV (FWHM)),
25 the photon energy of the excitation light with a maximized PL intensity is coincident
26 with the energy of the absorption edge (3.22 eV) in Phenomenon 1. This fact supports
27 the possibility that MW irradiation creates a new energy state at 3.22 eV.

28 If Phenomenon 1 of the absorption spectra and Phenomenon 3 of the PLE spectra
29 originate from the energy shift of the conduction band, the electron transition process
30 due to relaxation from the conduction band would not shift. However, excitation above
31 3.23 eV of the sample with MW irradiation actually shifts the broad peak, indicating
32 that the above assumption is incorrect. Hence Phenomena 1, 3, and 4 imply that MW
33 irradiation creates a new energy state at 3.22 eV, which is below the conduction band.

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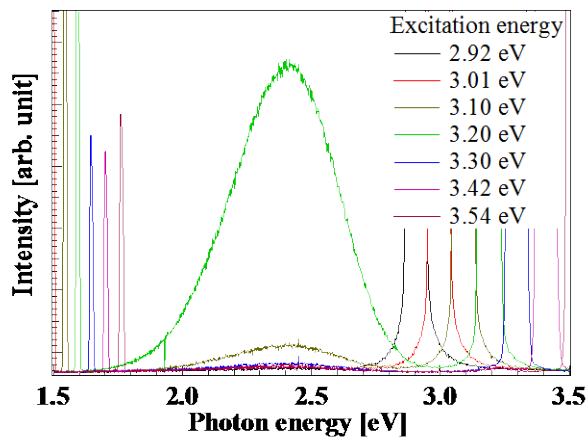


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2

3 Fig. 3. (a) PL spectra of ZnO sintered at 873 K without MW irradiation
 4 (b) The intensity of the second order diffraction of the excitation light with
 5 3.54 eV (350 nm) in the case of TiO₂ and ZnO without MW irradiation.



6

7

Fig. 4. PL spectra of ZnO sintered at 873 K with MW irradiation

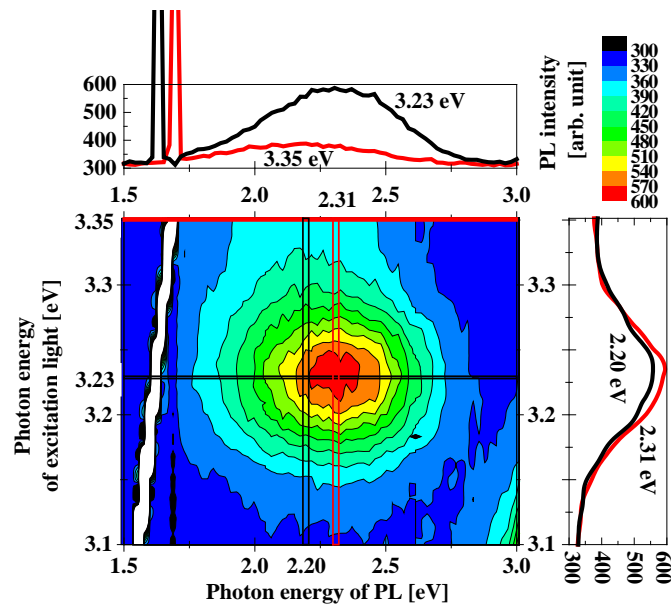


Fig. 5. PLE spectra of ZnO sintered at 873 K with MW irradiation

3.3 PL spectra at low temperature

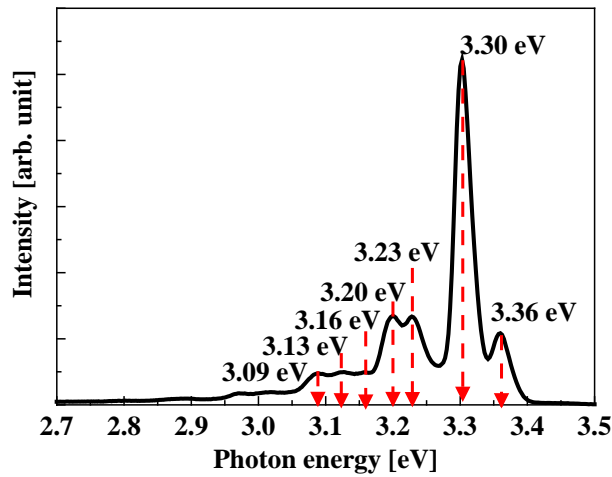
PL measurements using a He-Cd laser at low temperature were conducted to understand the electronic structure near the bandgap energy. A band-edge emission with several peaks is observed in the specimen without MW irradiation (Fig. 6), and the center energies of those peaks were 3.36 eV, 3.30 eV, 3.23 eV, 3.20 eV, 3.16 eV, 3.13 eV, and 3.09 eV (Phenomenon 5). The peaks appear in intervals of 0.07 eV (3.23 eV \rightarrow 3.16 eV) and about 0.10 eV (3.30 eV \rightarrow 3.20 eV \rightarrow 3.09 eV, or 3.23 eV \rightarrow 3.13 eV). The peaks at 3.36 eV, 3.30 eV and 3.23 eV in Fig. 7 are assigned to the exciton bound to an ionized donor, a two-electron transition of an exciton bound to a neutral donor, and a donor to an acceptor pair transition (DAP), respectively [28]. This spectrum is a typical phonon replica, and peaks appearing at 0.07 eV intervals have been attributed to the phonon replicas of the longitudinal optical mode, while peaks appearing at 0.10 eV intervals have been reported as the phonon replica induced by two phonons of the transverse optical phonon [28]. A phonon replica is observed in the PL spectrum of a material with a high purity and a low defect density because the PL spectrum of a material with low purity and high defect density is dominated by the emission from the defect level [29]. Therefore, these results confirm that the specimen without MW irradiation has a high purity and low defect density.

On the other hand, the band-edge emission of the ZnO with MW irradiation (Fig. 7) has two peaks with energies of 3.36 eV and 3.32 eV (Phenomenon 6), and a phonon replica is not observed in case of the PL spectrum with MW irradiation. The peak at 3.32 eV is assigned as excitons bound to Zn vacancy [30]. Therefore, these observations

1 demonstrate that the MW irradiation creates Zn-vacancy defects in ZnO.

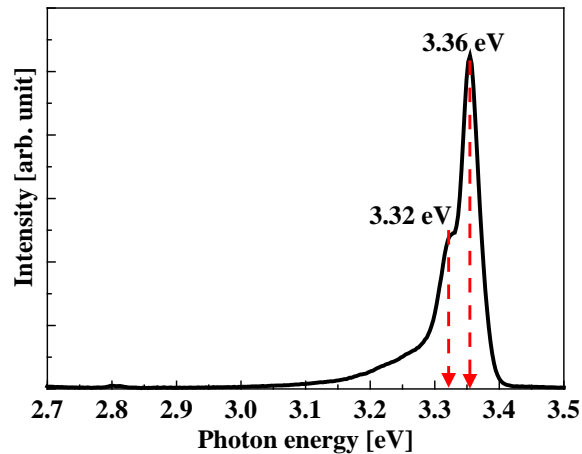
2 Both specimens with and without MW irradiation show an exciton emission at 3.36 eV
 3 (Figs. 6 and 7). Because the exciton emission of each specimen is coincident with each
 4 other [31], MW irradiation does not change the band structure outside of the bandgap.
 5 Therefore, these results are also consistent with the creation of a new energy state
 6 between the conduction and valance bands due to MW irradiation (Section 3.2).

7



8

9 Fig. 6. PL spectra using a He-Cd laser (325 nm, 3.81 eV) at low temperature (14 K)
 10 on the surface of ZnO without MW irradiation



11

12 Fig. 7. PL spectra using a He-Cd laser (325 nm, 3.81 eV) at low temperature (14 K)
 13 on the surface of ZnO with MW irradiation

14

15 3.4 Electronic structures of ZnO with and without MW irradiation

16

Figure 8 (a) and (b) show the energy diagram with and without MW irradiation at

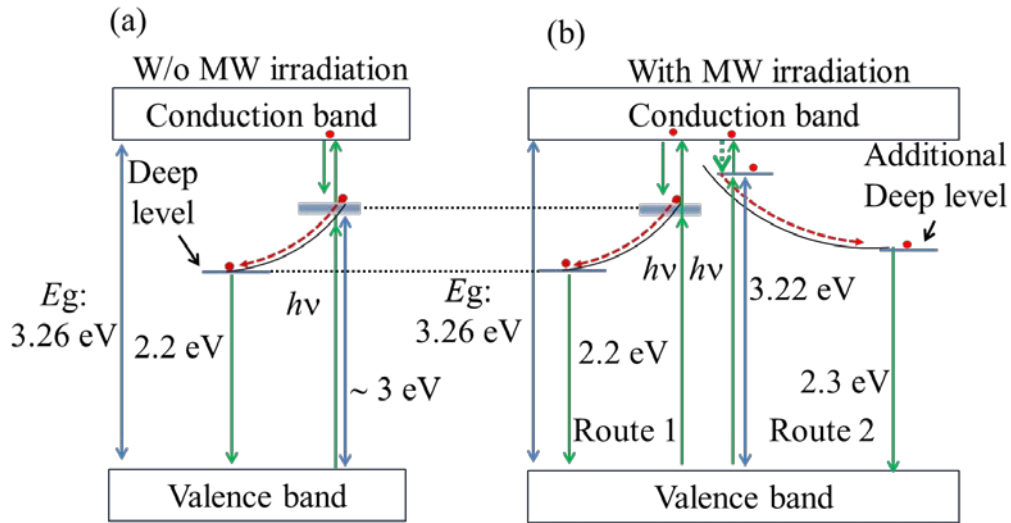
1 room temperature, respectively. The band at 2.20 eV in Fig.3 reportedly originates from
2 the defect level [22, 24, 26]. In addition, the broad PL emission band, which is observed
3 for all excitation energies (2.92–3.42 eV) is similar to the case for a large Stokes-shift
4 PL. Therefore, the PL band at 2.20 eV is a typical thermal creation of the deep level
5 with a large lattice relaxation, and the electron is trapped around 3 eV. The fact that the
6 PL intensity is independent of the excitation energy suggests that the trap level has a
7 defined width (Fig. 8 (a)). Moreover, there is not an energy difference in the band-edge
8 emissions between the two specimens at low temperature, suggesting that the bandgap
9 energy at room temperature is 3.26 eV for both specimens.

10 On the other hand, for ZnO with MW irradiation, an additional energy state is created
11 near the conduction band due to the defect level generation by MW irradiation, which
12 may be attributed to the plasma emission such as a zinc plasma and an oxygen plasma
13 by MW irradiation or to the thermal effect induced by MW heating. Because, in the
14 previous reports [13, 14], the plasma emission of zinc atom and oxygen atom was
15 observed by microwave irradiation, and it shows that atoms of zinc and oxygen in ZnO
16 are emitted from the sample. Therefore, this phenomenon shows the possibility that
17 defects are created by the evaporation of the zinc atom and oxygen as plasma. In
18 addition, the plasma emission shows that the sample was heated at high temperature
19 over 2000 °C because the temperature around 2000°C is needed for decomposition,
20 which is required to observe the plasma [13]. It is reported that defects are created when
21 the sintering temperature is over 750 °C [32]. When the sample was partially heated over
22 2000°C by MW irradiation, temperature of the rest of the sample is also elevated to
23 enough high temperature for defect creation. Therefore, as the second candidate of the
24 cause of the defect creation, it is considered that defects are created by the thermal
25 effect. However, additional investigations are required to clarify the detailed mechanism
26 of the defect generation.

27 Because the band of the peak at 2.31 eV in Fig.5 is also broad, the additional energy
28 state by MW irradiation is also at a deep level with large lattice relaxation. In addition,
29 the maximized intensity of the PL at a particular excitation energy (3.23 eV) and the
30 absorption edge at 3.22 eV suggest that a clear trap level is generated around 3.22 eV.

31 In the case of the sample with MW irradiation, two route of the electron transition
32 were considered (Fig.8 (b)). In Route 1 an electron transition occurs via the trap level.
33 In Route 2 an electron transition occurs via a trap level at 3.22 eV. Because the peak of
34 the band shifts from 2.31 eV to 2.20 eV, it is possible that the probability of the electron
35 transition from the conduction band to the trap level at 3.22 eV is lower than that from
36 conduction band to the trap level near 3 eV (i.e., once electron is excited to the

1 conduction band, Route 1 is favored to Route 2). These results indicate that MW
 2 irradiation in ZnO creates a new energy state and modifies the electronic structure.



3

4 Fig.8 Schematic of the ZnO energy diagram at room temperature: (a) without and (b)
 5 with MW irradiation

6

7

8 4. Conclusion

9 It was confirmed that MW irradiation affected the bandgap electronic structure of ZnO,
 10 through conventional absorption spectroscopy, photoluminescence spectroscopy and
 11 photoluminescence excitation spectroscopy by an ultraviolet synchrotron light source. A
 12 new defect energy state slightly below (~ 0.04 eV) bandgap energy is created as a
 13 shallow energy level by MW irradiation to ZnO. The new MW irradiation-induced
 14 defects also alter the electron transition process. These findings indicate that this type of
 15 bandgap should allow a higher conductivity, which will enhance microwave-material
 16 interactions.

17

1 **5. Acknowledgment**

2 This work was partly supported by the “Energy Science in the Age of Global Warming”
3 of Global Center of Excellence (G-COE) program (J-051). The PL and PLE
4 measurements were supported by the Use-of-UVSOR Facility Program (BL7B 2012–
5 2013) of the Institute for Molecular Science, Japan. We would like to thank all the staff
6 members of the UVSOR facility. Part of this study was supported by a Grant-in-Aid for
7 Scientific Research (C) (23561030) from the Japan Society for the Promotion of
8 Science.

9

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