# 論文 / 著書情報
# Article / Book Information

| | |
|---|---|
| Title | Effect of MgZnO-layer capping on optical properties of ZnO epitaxial layers |
| Authors | T. Makino,K. Tamura,C. H. Chia,Y. Segawa,M. Kawasaki,A. Ohtomo,H. Koinuma |
| Citation | Applied Physics Letters, Vol. 81, No. 12, |
| Pub. date | 2002, 9 |
| URL | http://scitation.aip.org/content/aip/journal/apl |
| Copyright | Copyright (c) 2002 American Institute of Physics |

# Effect of MgZnO-layer capping on optical properties of ZnO epitaxial layers

T. Makino,[a] K. Tamura,[b] C. H. Chia,[c] and Y. Segawa[c]
*Photodynamics Research Center, Institute of Physical and Chemical Research (RIKEN), Sendai 980-0845, Japan*

M. Kawasaki[d] and A. Ohtomo
*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

H. Koinuma[d]
*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*

(Received 13 May 2002; accepted for publication 18 July 2002)

Photoluminescence (PL) and reflectivity spectra of ZnO epilayers capped with $Mg_xZn_{1-x}O$ layers (up to $x=0.36$) are reported. These capped films were epitaxially grown on lattice-matched $ScAlMgO_4$ substrates by laser molecular-beam epitaxy. A photoluminescence spectrum from the ZnO layer taken at 5 K shows emission bands at 3.389, 3.376, and 3.362 eV. The two higher bands are due to *A*- and *B*-free exciton emissions and the lowest band is due to emission of a neutral-acceptor bound exciton ($I_6$). The linewidth of the $I_6$ emission in our uncapped sample (0.8 meV) is significantly smaller than that in the capped one (6 meV). This is probably due to strain applied across the ZnO layer because of the difference in lattice constant between the two layers. The spectral assignment of the free exciton emissions is strengthened by a comparison with a temperature-dependent PL study and a reflectivity study. With an increase in temperature, the intensity of the bound exciton emission line decreased drastically and became comparable to that of free exciton lines. Free exciton emissions are already detectable at the liquid He temperature for the capped samples, which is never achieved in the uncapped ones grown under identical conditions. This indicates the high degree of purity of the capped films. © *2002 American Institute of Physics*. [DOI: 10.1063/1.1506783]

Zinc oxide is a II–VI semiconductor compound with a large band gap ≈3.4 eV and a strong excitonic structure near the three-dimensional $M_0$ critical point even at room temperature. It is an attractive material for many applications in optics, optoelectronics, and surface acoustic wave modulators.[1] Although much effort has recently been devoted to seeking a suitable buffer layer for ZnO epitaxy, the effects of capping on its optical properties have not been extensively investigated.[2]

As can be understood by giving examples of quantum wells, it is one of the key issues in growing ZnO that has a flat surface. Establishment of a technique so that different material can be deposited without inducing degradation is also important. The advantage of capping has been confirmed in other semiconductors, e.g., III–V materials. It is widely known that the optical properties of GaAs epilayers can be improved by capping with AlGaAs layers (see, e.g., Ref. 3). Here we seek a suitable material as a capping layer for ZnO. It is desired that the material is transparent in the wavelength region of interest and that it can be deposited without inducing degradation. This research work is the first step toward this goal.

A solid solution of $Mg_xZn_{1-x}O$ whose band gap is larger is expected to be one of the best candidates for this, because its lattice constant is close to that of ZnO. This is also due to the negligibly small interdiffusion coefficients of Mg between these two layers.[4] It has already been used as a barrier layer in ZnO-based quantum wells. In this letter, we compare the optical properties of capped ZnO epilayers with those of an uncapped one studied by photoluminescence (PL) and reflection spectroscopies.

We measured these optical spectra in 12-nm-thick ZnO epilayers capped with 50-nm-thick $Mg_xZn_{1-x}O$,[5] which were grown on $ScAlMgO_4$ (SCAM) substrates by laser molecular-beam epitaxy (LMBE). The capping layer was made thicker than the ZnO layer in order to make the influence of the capping more serious. One can find a detailed description of the sample specifications grown with LMBE in Refs. 6–8. The SCAM(0001) substrate has hexagonal lattice constants $a=3.246$ Å and $c=25.195$ Å with in-plane lattice mismatch as small as 0.09% for ZnO. The growth temperature and partial oxygen pressure were 500 °C and $10^{-5}$ Torr, respectively.

The Mg concentrations of the capping layers corresponding to these nine ZnO samples were $x=0.09$, 0.13, 0.15, 0.20, 0.21, 0.22, 0.31, and 0.36, respectively. The thickness of ZnO was 12 nm. A weak continuous wave (cw) He–Cd laser of 325.0 nm (5 mW) was used for the PL measurements. Reflection measurements were carried out using a Xe arc lamp as a light-emitting source, which provided ample continuum in the spectral region of interest.

Figure 1 shows a typical PL spectrum of the capped film ($x=0.15$) in the exciton resonance region of ZnO taken at 5

[a]Electronic mail: tmakino@postman.riken.go.jp
[b]Also at Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan.
[c]Also at Department of Physics, Tohoku University, Sendai 980-8578, Japan.
[d]Also at: Cominatorial Materials Exploration and Technology, Tsukuba 05-004, Japan.

 

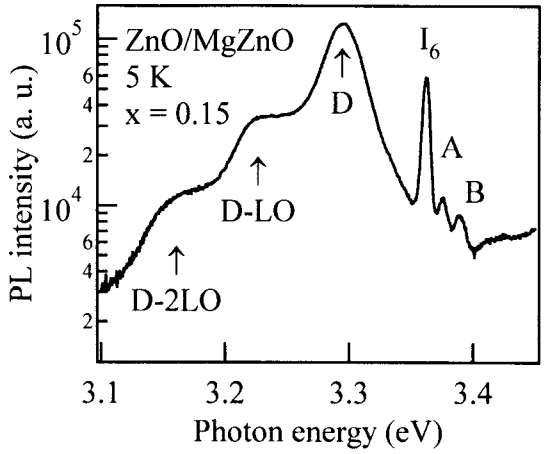


FIG. 1. Photoluminescence spectra of a ZnO epilayer capped with $Mg_{0.15}Zn_{0.85}O$ taken at 5 K in the ZnO exciton resonance region. The spectrum is on a logarithmic scale. The full width at half maximum (FWHM) of the bound exciton emission band is estimated to be 6 meV. $I_6$ is the resonance energy position of an exciton bound to a neutral donor.

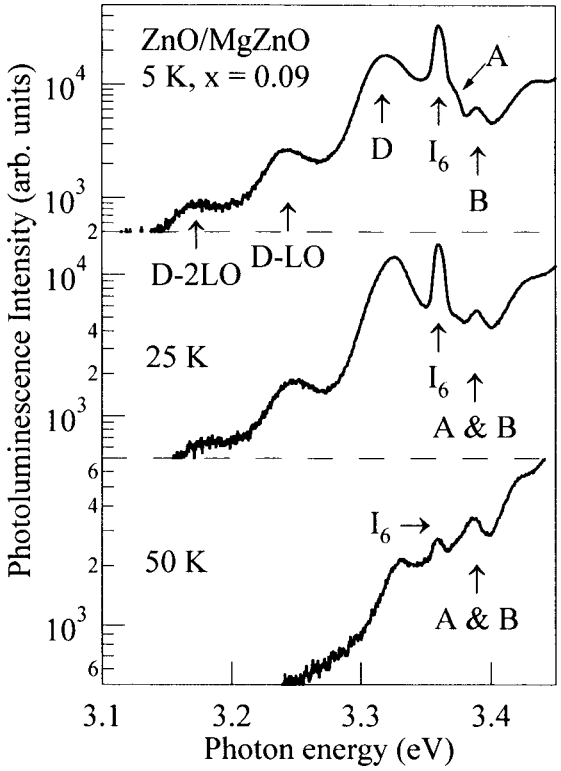


FIG. 2. Photoluminescence spectra of the sample with Mg concentration $x = 0.09$ taken at various temperatures. The temperatures measured are shown.

K on a logarithmic scale. Emission from the MgZnO cap layer peaking at 3.65 eV is not shown. Two free exciton emissions at 3.376 eV (*A*, the *A* exciton) and 3.389 eV (*B*, the *B* exciton) are confirmed. Emission of neutral-acceptor bound exciton at 3.362 eV ($I_6$) is dominant in the spectrum. There is much stronger emission from the alloyed capping layer because of its larger thickness. Spectral assignment is done by a comparison with the reflectivity spectra in the exciton resonance region of ZnO. The linewidth of the $I_6$ emission in our uncapped sample (0.8 meV) is significantly smaller than that in the capped one (6 meV). This is probably due to strain applied across the ZnO layer because of the difference in lattice constant between the two layers.[9] A *D* band (3.29 eV) accompanied by two optical-phonon replicas was also observed. This band is considered to be emitted from the capping layer because such emission could be observed in the MgZnO epilayers directly grown on sapphire (0001) substrates.[10] One cannot draw the conclusion that it is assigned to radiative recombination of the electron-hole pairs spatially separated due to quantum-confined Stark (or the piezoelectric and spontaneous polarization) effects. This band may originate from donor–acceptor pair luminescence from the *alloyed layer*.

The temperature-dependent behavior of PL spectra of the capped sample is shown in Fig. 2. As the temperature increases, the $I_6$ line decreases in intensity, thermally releasing excitons from the donor impurities. Then, free exciton emission arises somewhat. The PL spectra are normalized to the $I_6$ peak intensity. Another sample with Mg concentration of $x = 0.09$ is used in Fig. 2 in order to demonstrate that all the capped samples exhibit free exciton emission at 5 K. With a rise in temperature [cf. Figs. 2(b) and 2(c)], the free exciton emissions become relatively pronounced. The intensity of the free-exciton band finally becomes comparable with that of the $I_6$ band at temperatures higher than 50 K. This temperature-dependent PL study supports our spectral assignments for *A*- and *B*-free excitons. It was difficult to observe the free exciton emission around the liquid He temperature in the uncapped ZnO grown under almost identical conditions.[11] At higher temperatures, an increase in the luminescence intensity of free exciton emission can be expected due to the effect of the thermal release of bound excitons. The free exciton emissions already detectable at the liquid He temperature possibly indicate the high purity of our capped films and suppression of the creation of trapping centers, as has been admitted by the authors of Refs. 12 and 13.

Figure 3 shows a reflection spectrum in the other capped sample ($x = 0.2$) reflected from the ZnO layer. It should be noted that the exciton resonance region of the cap MgZnO layer is much higher than the energy range shown in Fig. 3. There is much information in Fig. 3. First we remark that the spectral positions of the *A* and the *B* excitons coincide with those confirmed in the PL spectra introduced above. The free exciton energies of this sample are significantly higher than those of ZnO bulk crystal[14] which is possibly due to the strain effect.[15,16] Lattice mismatch between MgZnO and ZnO layers may induce some strain inside the ZnO layer.[17] Below the *A*-exciton resonance energy, some oscillating structures are observed that are due to multiple reflection in the epilayer. This is an indication of a good epitaxial relation among ZnO, MgZnO, and $ScAlMgO_4$. The interference modes are superimposed on the oscillator structure observed around the *A*-exciton resonance region. It is well known that the rising behavior of the reflectivity line shape at energies higher than the *B*-longitudinal exciton position (shown by the dashed arrow in Fig. 3) is very sensitive to the damping parameter of excitons.[18,19] Although one can calculate the reflection spectra using a model such as the well-known polaritonic one, it is beyond the scope of our study. The damping parameter of the *B* exciton for the capped layer is smaller than or comparable to that of the uncapped layer because, in the former case, the reflectivity recovers more rapidly from its mini-

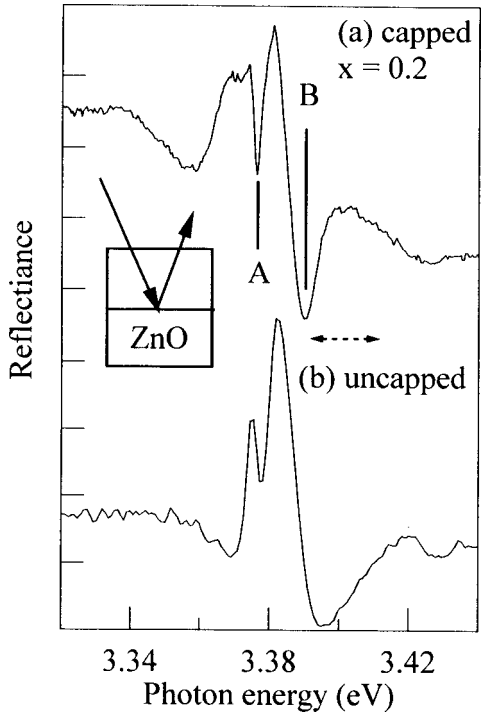


FIG. 3. Reflection spectra of a capped ZnO epilayer taken at 5 K in the ZnO exciton resonance region with Mg content $x=0.20$. The inset shows that the resonance structures displayed do not stem from the cap MgZnO layer but from the ZnO layer. Attention was paid to the energy region shown by the dashed arrow to compare the excitonic damping parameter between capped and uncapped films.

mum. The definition of the excitonic damping parameter was given in Ref. 20. Recently, line shape fitting of excitons which can give both the homogeneous and inhomogeneous broadening parameters for free exciton resonances was performed for ZnO films and reported in Ref. 21.

In summary, PL and reflectivity spectra of ZnO epilayers capped with $Mg_xZn_{1-x}O$ layers with wider band gaps (up to $x=0.36$) were reported. These capped films were epitaxially grown on SCAM(0001) substrates by laser molecular-beam epitaxy. Photoluminescence spectra of the ZnO layers taken at 5 K showed emission bands at 3.376, 3.389 and 3.362 eV, respectively. The two higher bands are due to free exciton emissions and the lowest one is due to emission of a bound exciton ($I_6$). The linewidth of $I_6$ emission in our capped sample (6 meV) is significantly larger than that in the uncapped one (0.8 meV). This is probably due to strain applied across the ZnO layer because of the difference in lattice constant between the two layers. By superimposing PL and reflectivity spectra, we associated the emission peaks at 3.376 and 3.389 eV to the transition energies of free excitons. The free exciton emissions can hardly be recognized in the uncapped ones grown under identical conditions. The free exciton emissions already detectable at the liquid He temperature indicate the high purity of our capped films, as was admitted by the authors of Refs. 12 and 13.

The authors would like to express their sincere gratitude to Robert Romestain for critical reading of the manuscript.

[1] C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lu, M. Wraback, and H. Shen, J. Appl. Phys. **85**, 2595 (1999).
[2] R. D. Vispute, V. Talyansky, S. Choopun, R. P. Sharma, T. Venkatesan, M. He, X. Tang, J. B. Halpern, M. G. Spencer, Y. X. Li, L. G. Salamanca-Riba, A. A. Iliadis, and K. A. Jones, Appl. Phys. Lett. **73**, 348 (1998).
[3] K. Akiyama, N. Tomita, Y. Nomura, and T. Isu, Appl. Phys. Lett. **75**, 475 (1999).
[4] A. Ohtomo, M. Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **75**, 980 (1999).
[5] T. Makino, G. Isoya, Y. Segawa, C. H. Chia, T. Yasuda, M. Kawasaki, A. Ohtomo, K. Tamura, Y. Matsumoto, and H. Koinuma, in *Proceedings of the 1st International Conference on Combinatorial and Composition Spread Techniques in Material and Device Development, San Jose*, edited by G. Jabbour (SPIE, Bellingham, WA, 2000), Vol. 3941, p. 28.
[6] Y. Matsumoto, M. Murakami, Z. W. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **38**, L603 (1999).
[7] A. Ohtomo, T. Makino, K. Tamura, Y. Matsumoto, Y. Segawa, Z. Tang, G. K. L. Wang, H. Koinuma, and M. Kawasaki, in Ref. 5, p. 70.
[8] H. Koinuma, M. Kawasaki, and M. Yoshimoto, Mater. Res. Soc. Symp. Proc. **397**, 145 (1996).
[9] T. Makino, N. T. Tuan, H. D. Sun, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 975 (2000).
[10] A. Ohtomo, Ph.D. thesis, Tokyo Institute of Technology, Tokyo, 2000.
[11] T. Makino, G. Isoya, Y. Segawa, C. H. Chia, T. Yasuda, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, J. Cryst. Growth **214/215**, 289 (2000).
[12] A. Zenner, H. Alves, D. M. Hofmann, B. K. Meyer, M. Heuken, J. Bläsing, and A. Krost, Appl. Phys. Lett. **80**, 2078 (2002).
[13] Y. F. Chen, H. K. Ko, S. Hong, and T. Yao, Appl. Phys. Lett. **76**, 559 (2000).
[14] W. Y. Liang and A. D. Yoffe, Phys. Rev. Lett. **20**, 59 (1968).
[15] B. Gil, Phys. Rev. B **64**, R201310 (2001).
[16] B. Gil, A. Lusson, V. Sallet, S.-A. Said-Hassani, R. Triboulet, and P. Bigenwald, Jpn. J. Appl. Phys., Part 2 **40**, L1089 (2001).
[17] T. Makino, Y. Segawa, A. Ohtomo, K. Tamura, T. Yasuda, M. Kawasaki, and H. Koinuma, Appl. Phys. Lett. **79**, 1282 (2001).
[18] T. Hayashi and M. Watanabe, Solid State Commun. **69**, 959 (1989).
[19] J. Lagois and K. Hümmer, Phys. Status Solidi B **72**, 393 (1975).
[20] R. J. Elliott, Phys. Rev. **108**, 1384 (1959).
[21] M. Zamfirescu, A. Kavokin, B. Gil, G. Malpuech, and M. Kaliteevski, Phys. Rev. B **65**, R161205 (2002).