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Invited

ZnO Quantum Structures towards UV Diode Lasers

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1. Introduction

Extensive research of high T_c superconducting thin films for more than 10 years has opened a door to new class of electronics in which versatile properties of epitaxial metal-oxide films and heterostructures play a major role [1]. As a photonic branch of **"oxide electronics"**, we have reported that ultraviolet (390 nm) laser emission could be realized at room temperature from ZnO thin films [2]. Four years of our research has revealed the followings [3].

Materials

- c-axis oriented ZnO epitaxially grows on sapphire (18% lattice mismatch). Here, epitaxial relationship holds only in rotational symmetry. There can be translationally incoherent grains [4]. Polarity in the growth direction is (000$\bar{1}$) [5].
- The size of grains can be controlled by taking nucleation and growth processes into account [6].
- Hexagonally shaped grains are closely packed and arraigned as honeycomb [4].
- Impurity, oxygen deficiency, crystallinity (stress, in- and out of plan mosaicness, grain-size) sensitively affect the emission property [6].

Physics

- Free exciton photoluminescence (PL) can be observed at room temperature because of very large exciton binding energy (60 meV) [2].
- Free exciton spontaneous, exciton-exciton spontaneous, exciton-exciton stimulated and electron-hole plasma stimulated emissions were seen as increasing the optical pumping intensity [2].
- The incoherent grain boundaries serve as mirrors to form longitudinal cavity --- it is not necessary to make artificial mirrors for laser [7].
- There is optimum crystal size (50 nm) for excitonic lasing (physics is not understood, yet) [8].

Besides such interesting findings of science, we have to solve many problems for bringing epitaxial metal-oxides to technologically competitive stage. As one of possible devices made out of ZnO, we have been developing technology towards ultraviolet laser diode. Bandgap engineering and p-type doping are two crucial factors for this purpose.

In this talk, we summarize aforementioned materials and physics issues of ZnO excitonic lasing and present further progress on former topic, i.e., bandgap engineering (3 to 4 eV) of ZnO by alloying with CdO or MgO [9] and fabrication of superlattices composed of them.

2. Bandgap Engineering

Epitaxial thin films were grown by pulsed laser deposition method with using ultra-high vacuum background. Sintered ceramics targets of pure ZnO (99.999 % purity) and those mixed with CdO or MgO were ablated by excimer laser pulses to evaporate the materials. Films were grown on sapphire (0001) substrates at about 500 °C and 10^{-6} Torr of oxygen.

All the films grew in an epitaxy fashion with high crystallinity. The composition of Cd or Mg in the alloy films were not identical to those in the target. The difference in vapor pressure (CdO > ZnO > MgO) causes the dilution of Cd and concentration of Mg in alloy films. Nevertheless, we could fabricate up to $Zn_{0.93}Cd_{0.07}O$ and $Mg_{0.33}Zn_{0.67}O$, which have band gaps of 3.0 and 4.0 eV, respectively. The PL absorption spectra of the alloy films are presented in Fig. 1. As can be clearly seen, PL peak shifts depending on the film composition.

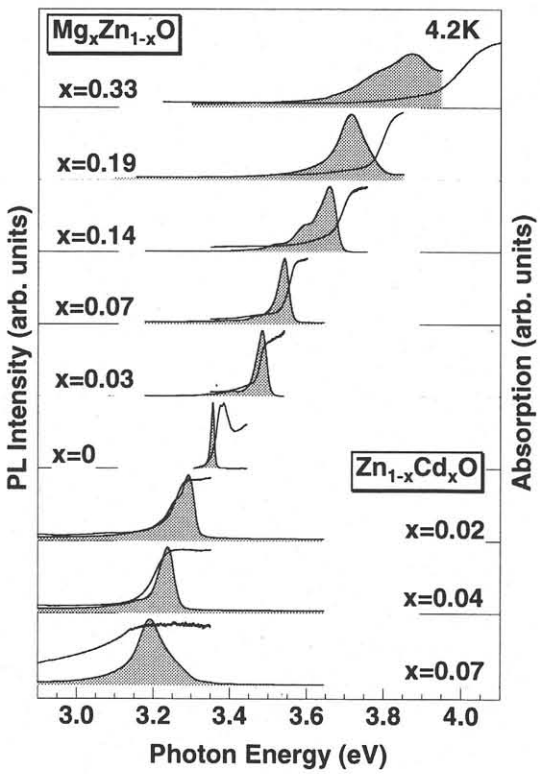

Fig. 1 Absorption and PL spectra of MgO-ZnO and ZnO-CdO alloy films.

Figure 2 shows lattice parameters (in-plane: a-axis and out of plane: c-axis in the wurtzite structure) measured for thick and therefore relaxed alloy films. The c-axis length has monotonous variation, which is consistent with the change of average ionic radius. However, the a-axis length has its minimum for pure ZnO. The increase of the a-axis for $Mg_xZn_{1-x}O$ alloys can be understood as the increase of average ionicity of the compound induces internal strain (decrease of c and increase of a) so as to minimize static Coulomb energy. This fact implies important conclusion; there can be perfectly lattice matched superlattices in $Mg_yZn_{1-y}O/Cd_xZn_{1-x}O$, where piezoelectric effect in the strained superlattices can be neglected.

3. Superlattices

We have grown superlattices composed of pure ZnO and $Mg_{0.2}Zn_{0.8}O$. In order to get smooth surface of the films, it was crucially important to grow buffer ZnO (100 nm) on sapphire substrate prior to the superlattice formation. The layer thickness of superlattices were controlled by the deposition time.

X-ray diffraction, cross sectional transmission microscope, Auger depth profiling clearly indicate the periodic structure of the superlattices as designed. Figure 3 shows PL and excitation (PLE) spectra for ZnO and superlattices with various well layer thickness. As decreasing well layer thickness, PL peak shifts to higher energy side. Since the PLE spectra have a second peak where carrier excitation at the barrier layers should take place, we conclude superlattices of abrupt interface are fabricated to show quantum confinement effect.

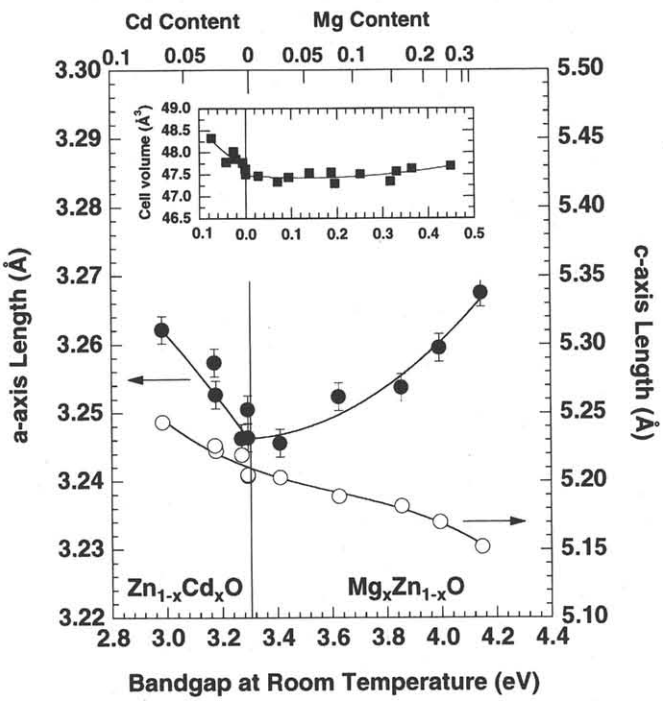

Fig. 2 Lattice Paranmeters of MgZnO and ZnCdO alloy films. Inset shows cell volume of the alloys.

4. Summary

These phenomena and technological issues are important and on the traditional track of the progress in semiconductor technology. Moreover we shall note the following fact; ZnO is one of the materials which have the longest and most extensive history of research among oxides for such applications as transducer, catalyst, transparent conducting film, and surface acoustic devices. It was surprising for us to find out a novel function in such an old matter. One can say that such a new processing tool as laser MBE gave a new life to an old material. There should be other oxides which may explore exotic properties but so far cannot because of poor quality of epitaxial films.

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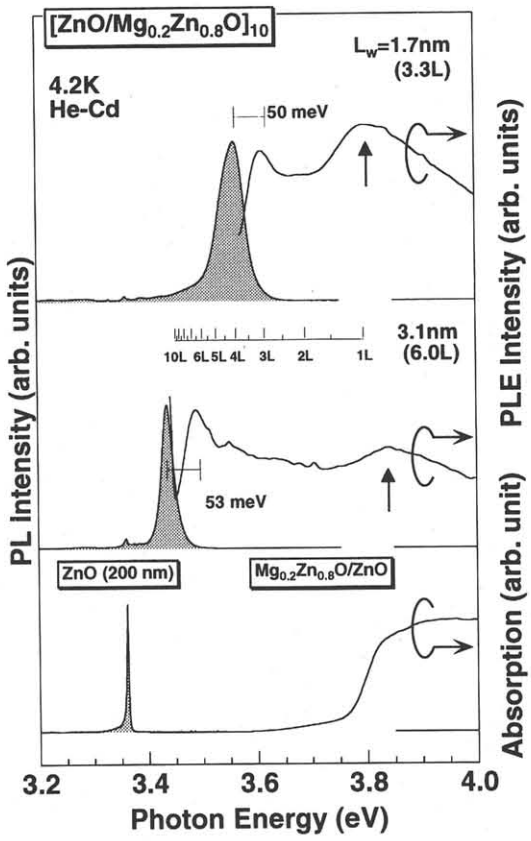

Fig. 3 Photoluminescence and excitation spectra of $ZnO/Mg_{0.2}Zn_{0.8}O$ superlattices. Arrows indicates carrier generation at the barrier layers.