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Photoluminescence properties of ZnO epitaxial layers grown on lattice-matched ScAlMgO$_4$ substrates

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Photoluminescence (PL) properties of ZnO films grown epitaxially on lattice-matched ScAlMgO$_4$ substrates are investigated. PL spectra of ZnO layers measured at 5 K are dominated by neutral-acceptor bound exciton emission at 3.359 eV (I_6) with a linewidth of 0.8 meV. Free exciton emission develops as temperature is raised and eventually dominates at temperatures higher than 120 K. Temperature dependence of intensity of the free exciton emission is discussed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1519336]

I. INTRODUCTION

The optical properties of wide band-gap semiconductors are currently the subject of many investigations, in response to the industrial demand for optoelectronic devices that can operate at short wavelengths. Zinc oxide is an interesting II–VI wurtzitic semiconductor which has a direct band gap of 3.37 eV. The excitonic binding energy is rather large; it turns out to be as large as 59 meV.[1] Such a large binding energy permits excitonic recombination well above room temperature (RT). The laser oscillation has been confirmed[2–4] well above RT in ZnO epilayers grown on sapphire (0001) substrates. This peculiar feature has prompted interests in the epitaxy of ZnO, resulting in a large number of publications devoted to this subject. However, detailed structural characterization by x-ray diffraction indicated the presence of large residual strain and structural defects in these epilayers. This results from the large lattice mismatch between the epilayer and the substrate. Several efforts are currently being made to improve the crystallinity by introducing MgO buffer layers[5] or by adopting MgAl$_2$O$_4$(111) substrates.[6] The difference between the lattice constants of these materials and ZnO is significantly smaller than that between sapphire and ZnO. ScAlMgO$_4$ (SCAM) is a more desirable substrate from the viewpoint of lattice matching because the misfit with ZnO is as small as 0.09%.

Ohtomo *et al.*[7] reported on the fundamental properties of these ZnO epilayers grown on lattice-matched SCAM substrates by laser-molecular-beam epitaxy (L-MBE). By comparing the full width at half maximum (FWHM) of the x-ray rocking curves, it was confirmed that using the SCAM substrates greatly improved the crystallinity of the epilayers.[7] The films also have high carrier mobility (100 cm^2/V s) and low residual carrier concentration (10^{15} cm^3). Furthermore, the surfaces of these samples were very smooth.

The improvement of the sample quality was also confirmed by optical characterization. Makino *et al.* reported on the fundamental optical properties of these samples.[8] In ZnO, the difference of the two exciton resonance energies (corresponding to the *A* and *B* exciton states) is only 7 or 8 meV. These two excitonic peaks were clearly distinguished in the absorption spectrum measured at 4.2 K for bulk crystals.[9] On the other hand, this was not the case for the ZnO epilayers grown on sapphire substrates. These two peaks became too broad to be distinguished because the damping constant of the excitons became larger as a result of the inferior crystallinity, as mentioned earlier. Such undesired broadening could be avoided in ZnO epilayers on SCAM substrates. The FWHMs of the exciton absorption bands of these samples were similar to those of the bulk.[9]

In this article, an extension of our previous short letter,[8] we report the photoluminescence (PL) properties of ZnO epilayers grown on SCAM substrates. Unlike free exciton lu-

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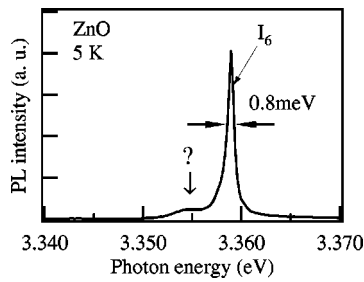
FIG. 1. PL spectra taken at 5 K in ZnO epitaxial layer. Emission line of the I_6 bound excitons is indicated by an arrow.

minescence, it is known that the FWHM of emission line of the bound exciton, which can be estimated from their PL spectra, reflects the degree of the inhomogeneity inside a sample. Therefore, the quality of a crystal can be judged by the FWHM. We describe further experimental evidence that supports the improvement of the optical properties of ZnO when using the lattice-matched substrates. We compare the linewidth of the bound-exciton emission bands in the PL spectra with the other published data obtained in various ZnO epilayers.[5,6] In addition, the temperature dependence of the PL properties is discussed.

II. EXPERIMENTAL PROCEDURES

The hexagonal SCAM (0001) substrate with lattice constants of $a = 3.246$ Å and $c = 25.195$ Å[10,11] has an in-plane lattice mismatch as small as 0.09% to that of ZnO. SCAM can be regarded as a natural superlattice composed of alternatively stacked layers of wurtzite (0001)-face $(Mg,Al)O_x$ and rocksalt(111)-face ScO_y. High quality single crystals can be grown by the Czochralski method.[10,11]

Epilayers of ZnO were grown on SCAM(0001) substrates by L-MBE under high vacuum conditions.[12] KrF excimer laser pulses were used to ablate ZnO ceramic targets, the purity of which was 99.999%. Growth temperature and partial pressure of oxygen were 550 °C and 1×10^{-6} Torr, respectively. These ZnO films have c-axis orientation. The PL spectra were measured using a continuous-wave He Cd laser (325 nm). The spectral resolution was less than 0.03 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of a ZnO film grown on a SCAM substrate taken at 5 K. An extrinsic feature dominates

TABLE I. Comparison of the FWHM for the bound excitonic emission taken at low temperatures T for various ZnO epitaxial layers. Assignment of each emission line is also shown: $(D\,^0X)$ and $(A\,^0X)$ are excitons bound to a neutral-donor and a neutral-acceptor, respectively.

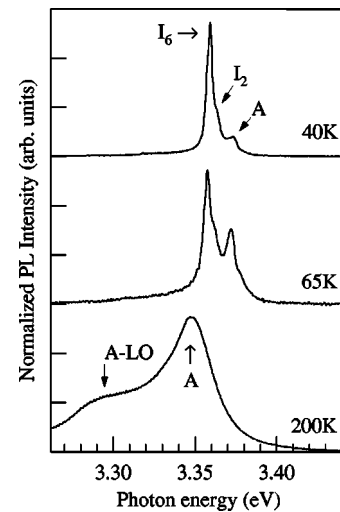| Substrates	Buffers	Assignment	FWHM (meV)	T (K)	Refs.
CaF_2	ZnO	$I_4\,(D\,^0X)$	12	10	14
Al_2O_3	MgO	$I_2\,(D\,^0X)$	3.2	4.2	5
$MgAl_2O_4$	none	$I_7\,(D\,^0X)$	2.5	4.2	6
Al_2O_3	none	$I_6\,(A\,^0X)$	5.1	4.2	15
$ScAlMgO_4$	none	$I_6\,(A\,^0X)$	0.8	5.0	This work

FIG. 2. PL spectra at various temperatures. Emission line of I_2 bound excitons and phonon replica (A-LO) are indicated by arrows.

the PL spectra. There are one dominant PL peak and a small shoulder. According to Tomzig and Helbig,[13] the luminescence band at 3.359 eV (denoted by I_6) corresponds to radiative recombination of excitons bound to neutral acceptors. Another shoulder (denoted by "?") was observed at ≈ 3.36 eV, the origin of which has not been clarified. It was found that the deep level emission was negligible. We compare the FWHMs of the bound exciton emission line with the values found in the literature.[5,6,14,15] These results are summarized in Table I. Assignment of each emission line is also shown. In Ref. 15, they probably made a mistake in the assignment of the emission line; the origin of this peak is from an exciton bound to a neutral acceptor like the assignment here. The FWHM of our sample was the smallest: it turns out to be 0.8 meV or less. For example, the FWHM of ZnO on sapphire substrates[15] is six times broader than that of our sample. In ZnO epilayers exhibiting the broadened emission lines,[5,6,14,15] microscopic fluctuation effects of strain distribution, the impurity and defect densities may induce potentials in which excitons are somewhat localized. Hence, these kinds of inhomogeneities contribute to the broadening of the bound exciton line. The low-energy tail extending from the bound excitonic emission peak due to the lattice deformation[5,6,14,15] is greatly reduced in a ZnO epilayer grown on SCAM, which possibly evidences high purity and crystal quality. The sharp excitonic emission also suggests the absence of grain boundary distribution. Indeed, room-temperature Hall measurement[7] indicates that the film has Hall mobility (100 cm^2/V s) and n-type residual carrier concentration (10^{15} cm^3).

As temperature increases, the I_6 line decreases in intensity, thermally releasing excitons from the impurities. Then, free exciton emission grows up with the increase of temperature. Temperature dependent behavior of PL spectra is shown in Fig. 2. These spectra are normalized so that the strongest peaks are of the same intensity. When the temperature increases ($\geqslant 30$ K), a new emission band arises on the higher energy side of I_6. This corresponds to radiative recombination of the A excitons. The intensity of the A exciton emis-
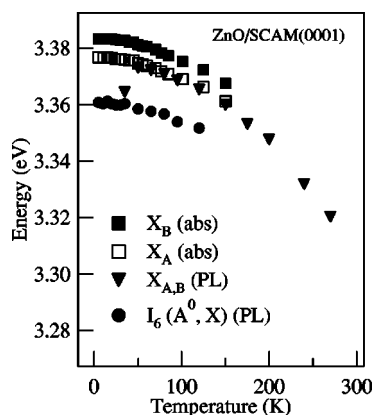
FIG. 3. Temperature dependence of the emission energies of a ZnO film for free exciton (closed triangles) and for neutral acceptor bound exciton (I_6, closed circles). Temperature dependences of the absorption energies for A free exciton (open squares) and for B exciton (closed squares) are shown for comparison (see Ref. 8).

sion line becomes much larger than that of I_6 at temperatures ≥ 120 K. An emission line (denoted I_2) was observed at temperatures ≥ 40 K. The peak energy of this band is 3.363 eV. Judging from its energy position, this is assigned to the radiative recombination of excitons bound to a neutral donor.[13,16] The luminescence band denoted by A-LO is radiative recombination of the A-free excitons with simultaneous creation of longitudinal-optical (LO) phonon (i.e., the phonon side band). The energy difference between the A and the A LO bands is equal to the energy of the optical phonon of ZnO (72 meV). At higher temperatures (above 120 K), the free exciton luminescence quenches gradually.

The peak positions of the observed excitonic emission lines are plotted against temperature in Fig. 3. Temperature dependences of the absorption energies for A free exciton (open squares) and for B exciton (closed squares) are shown for comparison.[8] By comparing the energies of emission and absorption, it is found that the emission peak denoted by a closed triangle here is due to radiative recombination of A free excitons.

Figure 4 shows temperature dependence of the free-exciton PL intensity in logarithmic scale. The experimental exponential decrease of the intensity with increasing tem-
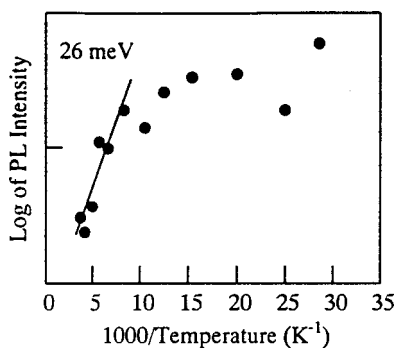
perature (≥ 100 K) enables us to evaluate the activation energy. One can deduce an activation energy which varies between about 10 and 60 meV, depending on the number of points which are considered for the slope estimation. It is hoped that more systematic studies for estimating an activation energy more precisely could be performed in the future.

IV. SUMMARY

Optical properties of the ZnO epilayers grown on SCAM substrates by L-MBE were investigated. This SCAM substrate was used to minimize the in-plane lattice mismatch between the epilayer and the substrate. Bound exciton emission at 3.359 eV (I_6) was dominant in PL spectrum taken at 5 K. We compared the linewidth of emission lines due to bound excitons with those of ZnO epilayers grown on various substrates or buffer layers.[5,6,14,15] As a result, the linewidth of our samples achieved the smallest record value of less than 0.8 meV, which possibly evidences high purity and crystal quality. Indeed, room-temperature Hall measurement[7] indicates that the film has Hall mobility (100 cm^2/V s) and n-type residual carrier concentration (10^{15} cm^3). Dominant luminescence of ZnO at high temperatures was due to the free exciton emission. The temperature dependence of the PL intensity was estimated.

ACKNOWLEDGMENTS

FIG. 4. PL intensity of the free-exciton band as a function of the measured temperature for our ZnO epitaxial layer.

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