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Contactless Electroreflectance Study of $Zn_{1-x}Mg_xO$

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Abstract

Contactless electroreflectance measurements at room temperature were used to determine the bandgap energies of $Zn_{1-x}Mg_xO$ thin films grown by metal-organic vapor phase epitaxy. It is found that the bandgap energy increases monotonically with the Mg composition x, up to the highest composition measured (x=0.45). The obtained correlation between the bandgap energy and the Mg composition can be used in the analysis of the electronic structure of $ZnO/Zn_{1-x}Mg_xO$ heterostructures at room temperature.

1. Introduction

ZnO, a wide-bandgap semiconductor with a bandgap energy of about 3.4 eV, is attracting much interest due to its large exciton binding energy and high bond strength, which are advantageous for optoelectronic applications [1-3]. It has been reported that the photoluminescence (PL) energy is increased to about 4 eV by alloying Mg into this material: as the Mg concentration x in $Zn_{1-x}Mg_xO$ increases from 0 to 0.5, the PL energy increases from 3.35 to 4.05 eV [4,5]. This has opened a new opportunity to fabricate $ZnO/Zn_{1-x}Mg_xO$ heterostructures for light emitters and ultraviolet photodetectors. $Zn_{1-x}Mg_xO$ in these structures is used as the barrier material to confine electrons and holes.

In designing the electronic properties of heterostructures, it is essential to know the band parameters, especially the bandgap energies, of the constituent semiconductors. PL measurements are routinely used to estimate the bandgap energies of these materials. However, there are significant drawbacks in using PL to determine the bandgap energies: usually the source of the luminescence is not the bandgap transition but exciton or impurity-related subbandgap transitions. When the origin of PL is not clear, the estimate of the bandgap energy from the measured PL energy could have a large uncertainty. In room-temperature measurements, the thermal broadening effect also contributes to the uncertainty. An alternative, and usually more precise, method of determining the bandgap energies is electroreflectance. In this technique, an ac electric field is applied to the sample and the modulation in the reflectance due to the electric field is spectroscopically measured to obtain derivative-like spectra. Since this technique directly probes the joint density of states of the material being studied, existence of impurity levels or nonradiative recombination centers hardly affects the spectra. Furthermore, unlike PL, it can be used to determine with high accuracy the critical point energies at room temperature. There are several methods to apply the electric field, and we used the contactless electroreflectance method pioneered by Pollak and coworkers [6]. The advantage of this method is that since no contact electrode is needed, the measurement is essentially nondestructive and leaves the sample unaltered. In this paper, we report on contactless electroreflectance measurements of the bandgap energies of $Zn_{1-x}Mg_xO$

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for x=0 to 0.45.

2. Experiment

$Zn_{1-x}Mg_xO$ films were grown on sapphire substrates using a horizontal-type metal-organic vapor phase epitaxy (MOVPE) system. Diethylzinc (DEZn), *bis*-cyclopentadienyli-Mg (cp_2Mg), and oxygen were usded as the reactants with argon as the carrier gas. The Mg content x depended on the cp_2Mg flow rate and the bubbler temperature which were in the range of 0-50 sccm and 30-40 ℃, respectively. Thin ZnO buffer layers were initially grown to improve the crystallinity of the $Zn_{1-x}Mg_xO$ layers. Details of the growth and characterizations of the films have been previously reported [3,5]. The composition of the films were estimated by energy-dispersive x-ray analysis and inductively-coupled plasma mass spectrometry.

Contactless electroreflectance measurements were taken at room temperature using a square wave of ±800 V at 1 kHz as the modulation potential. A 100 W xenon arc lamp combined with a Spex 270M monochromator with a 2400 grooves/mm grating was the light source.

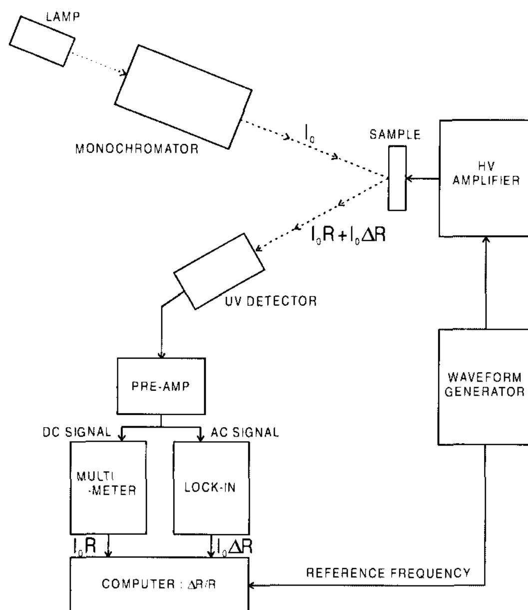

Fig. 1. Schematic diagram of the contactless electroreflectance setup.

A low-noise UV-grade silicon photodiode was used as the detector. The signal from the detector was amplified by a current preamplifier and the dc and ac components of the signal were recovered by a digital voltmeter and a lock-in amplifier, respectively. Fig. 1 shows the experimental setup schematically.

3. Results and Discussion

Figure 2 shows the electroreflectance spectra of a series of $Zn_{1-x}Mg_xO$ samples with various Mg compositions. Derivative-like features, characteristic of bandgaps, are seen. In order to extract the exact value of the bandgap energy from the spectra, the measured data are compared with a theoretical lineshape function. Since there is no indication of Franz-Keldysh oscillations in the spectra, the lineshape can be analyzed using the low-field approximation [7]. In this limit, the modulated reflectance ratio is given by

$$\frac{\Delta R}{R} = A \times Re[e^{i\phi}(E - E_g + i\Gamma)^{-m}] \qquad (1)$$

where E_g is the bandgap energy, Γ a broadening parameter, m a dimensionality parameter, ϕ a phase factor, and A the amplitude. The measured spectra can be fitted to Eq. (1) using E_g, Γ, m, ϕ, and A as the fitting parameters. When there are several critical points contributing to the electroreflectance signal, a linear combination of Eq. (1) can be used to account for different contributions.

In Fig. 2, the broken curves indicate the result of fits to the spectra using this method. Except for the spectrum for x=0 sample, two terms were needed to fit the data. The two terms correspond to the contributions of the $Zn_{1-x}Mg_xO$ layer and the ZnO buffer layer. The small vertical bars in Fig. 2 indicate the bandgap energy of the $Zn_{1-x}Mg_xO$ layer thus determined. The bandgap energy increases as the Mg concentration increases. Fig. 3 summarizes the band gap energies of $Zn_{1-x}Mg_xO$ and ZnO obtained from the samples. The error bars for the bandgap of ZnO bandgap energy are

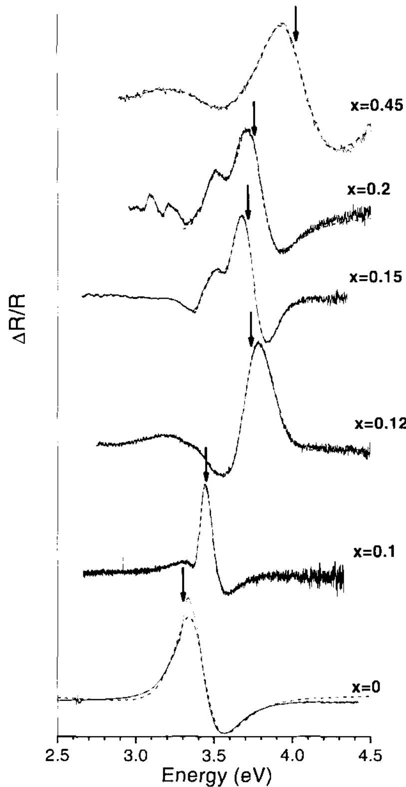

Fig. 2. Electroreflectance spectra of $Zn_{1-x}Mg_xO$ thin films. The broken lines are theoretical fits. The bandgap energies are indicated by vertical arrows.

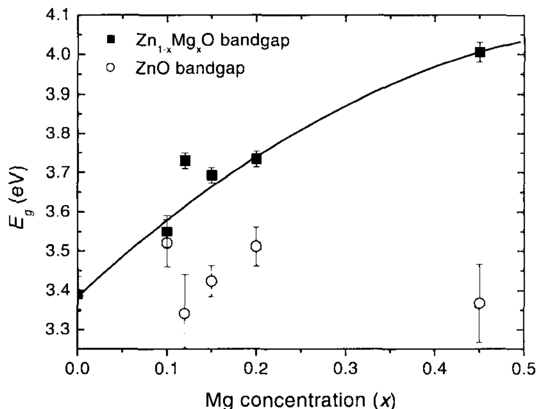

Fig. 3. Bandgap energies of the $Zn_{1-x}Mg_xO$ films and the ZnO buffer layers obtained from lineshape fitting. The curve is a quadratic fit to the $Zn_{1-x}Mg_xO$ excluding the data for the x=0.12 sample.

larger since the signal from the buried thin ZnO buffer layer is weaker than that from the $Zn_{1-x}Mg_xO$ layer because of the lower overall homogeneity of the buffer layers. The measured $Zn_{1-x}Mg_xO$ bandgap energy for the x=0.12 sample appears to be anomalously large; it is possible that because of the poor homogeneity of the sample the actual Mg composition of the sample is different from that of the piece used for the composition analysis. The curve in Fig. 3 indicates a least-squares quadratic fit to the data for the $Zn_{1-x}Mg_xO$ bandgap energy, excluding the x=0.12 sample. It is given by

$$E_g(x) = 3.38 + 2.11x - 1.62x^2 \text{ (eV)}. \qquad (2)$$

4. Conclusions

Contactless electroreflectance measurements at room temperature were used to determine the bandgap energies of $Zn_{1-x}Mg_xO$ thin films grown by MOVPE. The bandgap energy increases monotonically with the Mg composition x, up to the highest composition measured (x=0.45). The obtained E_g vs. x relation can be used in the analysis of the electronic structure of $ZnO/Zn_{1-x}Mg_xO$ heterostructures at room temperature.

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