p-type $Zn_{1-x}Mg_xO$ films with Sb doping by radio-frequency magnetron sputtering

Peng Wang,[a] Nuofu Chen,[b] Zhigang Yin, Ruixuan Dai, and Yiming Bai
Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

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Sb-doped $Zn_{1-x}Mg_xO$ films were grown on *c*-plane sapphire substrates by radio-frequency magnetron sputtering. The *p*-type conduction of the films ($0.05 \leqslant x \leqslant 0.13$) was confirmed by Hall measurements, revealing a hole concentration of $10^{15}-10^{16}\ cm^{-3}$ and a mobility of 0.6–4.5 $cm^2/V\ s$. A *p-n* homojunction comprising an undoped ZnO layer and an Sb-doped $Zn_{0.95}Mg_{0.05}O$ layer shows a typical rectifying characteristic. Sb-doped *p*-type $Zn_{1-x}Mg_xO$ films also exhibit a changeable wider band gap as a function of *x*, implying that they can probably be used for fabrication of ZnO-based quantum wells and ultraviolet optoelectronic devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2388254]

ZnO is regarded as a promising material for short wavelength light emitting diodes and laser diodes due to its direct wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature.[1,2] As a ternary alloy semiconductor, $Zn_{1-x}Mg_xO$ has a similar lattice constant to that of ZnO and a wider band gap than ZnO. Ohtomo *et al.* reported that the band gap of $Zn_{1-x}Mg_xO$ increased to 3.99 eV at room temperature with Mg content up to $x=0.33$.[3] Therefore ZnMgO is a suitable material for ZnO/ZnMgO superlattices, quantum wells, and ultraviolet (UV) optoelectronic devices. One of the critical issues in realizing such optoelectronic applications is to obtain high-quality and stable *p*-type doping. If a *p*-type ZnMgO is realized, the *p-n* junction will achieve a wider band gap that not only improves the efficiency of UV or blue light emitting devices even working at deep UV wave bands, but also creates application opportunities such as laser diodes in message storage.[4] Reports on *p*-type ZnMgO, however, are currently very limited. Only p-doped and N–Al-codoped *p*-type ZnMgO have been reported.[4,5]

In this letter, we report on the growth and properties of Sb-doped $Zn_{1-x}Mg_xO$ thin films with a series of Mg concentrations by radio-frequency (rf) magnetron sputtering. Room temperature Hall measurements show that *p*-type conduction can be realized in Sb-doped $Zn_{1-x}Mg_xO$ thin films with a variable band gap.

Sb-doped $Zn_{1-x}Mg_xO$ ($Zn_{1-x}Mg_xO:Sb$) thin films were grown on *c*-plane sapphire substrates, polished on both sides, by rf magnetron sputtering. The targets were fabricated by ZnO (99.99%) powder, mixing with MgO (99.99%) and Sb_2O_3 (99.99%). The atomic ratio of Zn/Mg was predetermined and variable, while the content of Sb in all the targets had the same value. The growth chamber exhibited a base pressure of 3×10^{-5} Pa. A pure Ar (99.999%) at a pressure of 0.4 Pa was used as the sputtering gas. The films (~300 nm in thickness) were deposited at 350 °C for 120 min. Following this, the as-grown films were annealed *in situ* at 600 °C in oxygen ambient for 60 min. The content *x* of Mg in $Zn_{1-x}Mg_xO:Sb$ films, determined by energy dispersive spectroscopy, are 0, 0.05, 0.08, 0.13, and 0.19. The content of Sb is about 0.02 in all the films.

The crystal structure of the films was determined by θ-2θ x-ray diffraction (XRD). The XRD patterns show only high intensity ZnO (000*l*) peaks in addition to an Al_2O_3 (0006) substrate peak, indicating that $Zn_{1-x}Mg_xO:Sb$ ($x \leqslant 0.19$) thin films have a single-phase wurtzite structure and a preferred orientation along the *c* axis. Because the nature of the XRD patterns is similar to each sample, only a typical XRD pattern for $Zn_{0.95}Mg_{0.05}O:Sb$ film is shown in Fig. 1. The *c*-axis length determined by XRD is plotted as a function of Mg content in the inset of Fig. 1. The *c*-axis length decreases slightly with increasing Mg content. The largest shift of the *c*-axis length is 0.56% for $x=0.19$, which is comparable to the experimental data in the previous reports.[3,6]

Figure 2 shows the transmittance spectra measured at room temperature by an ultraviolet-visible spectrometer. The average transmittance in the visible wavelength region is about 85% for all the films. It can be seen that the absorption edge of $Zn_{1-x}Mg_xO:Sb$ films continuously shifts to a shorter wavelength as the Mg content increases. The energy band

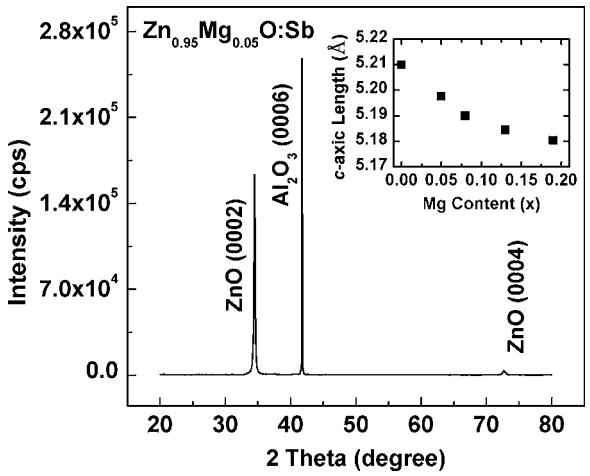

FIG. 1. XRD pattern of the $Zn_{0.95}Mg_{0.05}O:Sb$ film. The inset shows the *c*-axis lattice constant as a function of Mg content in $Zn_{1-x}Mg_xO:Sb$ films.

[a]Author to whom correspondence should be addressed; electronic mail: pwang@semi.ac.cn
[b]Also at National Laboratory of Micro-gravity, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, P. R. China.

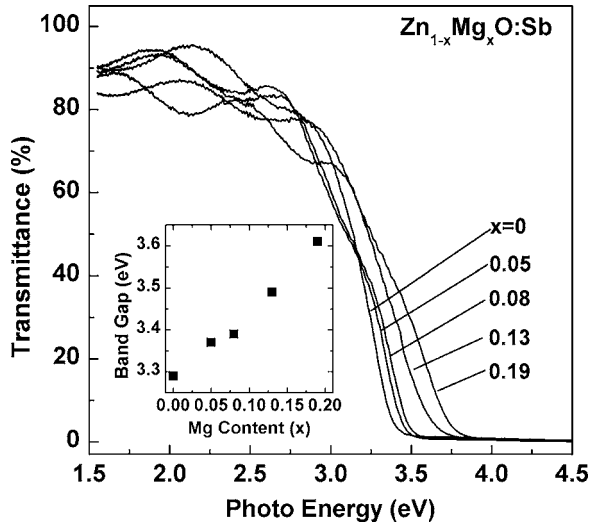

FIG. 2. Transmittance spectra of $Zn_{1-x}Mg_xO:Sb$ films ($0 \leqslant x \leqslant 0.19$) measured at room temperature. The inset shows the dependence of the band gap of $Zn_{1-x}Mg_xO:Sb$ films on Mg content.

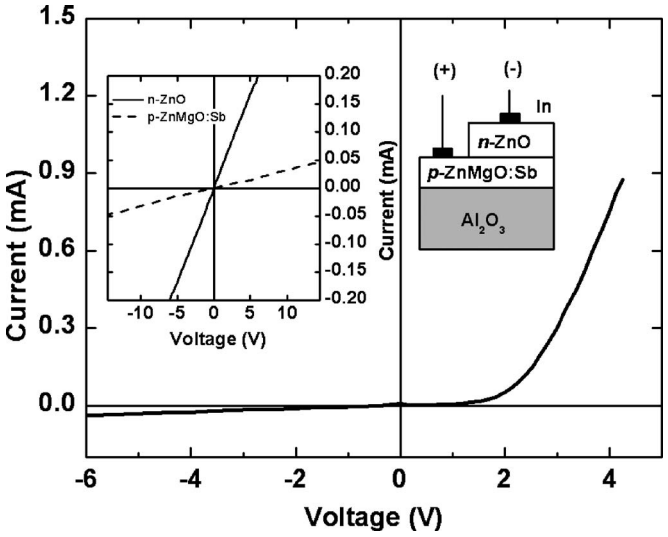

FIG. 3. *I-V* characteristics of a ZnO-based *p-n* homojunction (p-$Zn_{0.95}Mg_{0.05}O:Sb/n$-ZnO). The insets show the schematic structure of the *p-n* homojunction and the *I-V* characteristics of In contacts on *p*-ZnMgO:Sb and *n*-ZnO layers.

gap (E_g) is determined by extrapolating the plot of $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ is the photoenergy. As shown in the inset of Fig. 2, the band gap of $Zn_{1-x}Mg_xO:Sb$ increases gradually from 3.29 eV ($x=0$) to 3.61 eV ($x=0.19$), which is comparable to the value reported by Ohtomo *et al.*[3] and Makino *et al.*[7]

The electrical properties of $Zn_{1-x}Mg_xO:Sb$ thin films were investigated by Hall measurements using the four-probe van der Pauw configuration at room temperature. Table I shows the experimental data of samples with different x ranging from 0 to 0.13. The data of $Zn_{0.81}Mg_{0.19}O:Sb$ are not shown because a steady Hall voltage cannot be measured due to its high resistivity. For the ZnO:Sb film ($x=0$), only *n*-type conduction is obtained. This is consistent with our previous study,[8] which can be attributed to the strong self-compensation effect from a native shallow donor level[9] or H incorporation.[10] However, *p*-type conduction is achieved in $Zn_{1-x}Mg_xO:Sb$ films for $x=0.05$, 0.08, and 0.13. The $Zn_{0.95}Mg_{0.05}O:Sb$ film shows an optimized result with a hole concentration of 4.23×10^{16} cm^{-3}, a mobility of 4.5 cm^2/V s, and a resistivity of 32.9 Ω cm.

According to the results of Hall and UV-visible spectrometer measurements, the mechanism of *p*-type conduction in Sb-doped $Zn_{1-x}Mg_xO$ films can be explained tentatively. On the one hand, Sb is likely to serve as an acceptor in ZnO.[11,12] Xiu *et al.* reported on the fabrication of *p*-type Sb-doped ZnO, in which the acceptor energy level of Sb is estimated to be ~0.2 eV above the valence band.[11] Recently, Limpijumnong *et al.* proposed a doping mechanism for large-size-mismatched impurity Sb in ZnO, in which an $Sb_{Zn}-2V_{Zn}$ complex with lower formation energy can serve as a shallow acceptor in ZnO.[13] Moreover, O-rich growth or annealing conditions are required to obtain *p*-type ZnO, which agrees with recent observations.[5,11,14–17] On the other hand, the *n*-type background carriers generated by native donor defects are disadvantageous for *p*-type ZnO formation. It was reported that the addition of Mg in ZnO can shift the conduction band edge to a higher energy and increase the band gap, perhaps increasing the activation energy of the donor states and reducing the *n*-type background carrier concentration, which is very favorable for *p*-type conduction realization in $Zn_{1-x}Mg_xO$ films.[4,5] Therefore, the *p*-type films obtained in our work can be mainly attributed to two facts. Firstly, Sb dopants, acting as acceptors, provide the necessary hole carriers. Secondly, Mg doping increases the band gap and reduces the background electron concentration effectively.

TABLE I. Electrical properties of $Zn_{1-x}Mg_xO:Sb$ films ($0 \leqslant x \leqslant 0.13$).

Mg content x	Resistivity (Ω cm)	Hall mobility (cm^2/V s)	Carrier concentration (cm^{-3})	Conduction type
0	7.7	4	2.05×10^{17}	*n*
0.05	32.9	4.5	4.23×10^{16}	*p*
0.08	809.2	0.6	1.29×10^{16}	*p*
0.13	1031.5	1.5	4.02×10^{15}	*p*

The electrical properties of Sb-doped *p*-type $Zn_{1-x}Mg_xO$ films obtained in our work are very stable, even after five months. To further confirm the *p*-type conduction in Sb-doped ZnMgO films, a ZnO-based *p-n* homojunction was fabricated. As illustrated in the right inset of Fig. 3, a 300 nm Sb-doped $Zn_{0.95}Mg_{0.05}O$ layer with a hole concentration of ~10^{16} cm^{-3} was grown on a sapphire substrate, followed by a 300 nm undoped ZnO layer with an electron concentration of ~10^{17} cm^{-3}. Indium electrodes annealed at 400 °C were used to form Ohmic contacts to both the *p*-type and *n*-type ZnO layers. As shown in Fig. 3, the current-voltage (*I-V*) characteristic of the *p-n* homojunction exhibits a clear rectifying behavior. The turn-on voltage is ~2 V, which is consistent with the previous reports.[18,19] The left inset of Fig. 3 shows the *I-V* curves measured for a pair of contacts on the *p*-type and *n*-type ZnO layers. The linear behavior indicates that Ohmic contact to the electrodes is realized. These results confirm that the rectifying behavior shown in Fig. 3 is due to the ZnO-based *p-n* homojunction. During *I-V* measurements, no luminescence was observed under the forward bias because of the nonradiative recombination from defects in the interface of the junction and the low mobility of the *p*-ZnO layer.[20,21]

In summary, Sb-doped $Zn_{1-x}Mg_xO$ ($x \leqslant 0.19$) thin films have been grown on sapphire substrates via rf magnetron sputtering. The energy of the band gap systematically changed from 3.29 eV ($x=0$) to 3.61 eV ($x=0.19$). Room temperature Hall measurements show that the Sb-doped $Zn_{1-x}Mg_xO$ films ($0.05 \leqslant x \leqslant 0.13$) have *p*-type conduction. In addition, a ZnO-based *p-n* homojunction was fabricated, which showed a clear rectifying behavior. Our results indicate that Sb-doped *p*-type $Zn_{1-x}Mg_xO$ films with a variable band gap can probably be used for fabrication of ZnO-based quantum wells and ultraviolet optoelectronic devices.

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