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Comprehensive study of the *p*-type conductivity formation in radio frequency magnetron sputtered arsenic-doped ZnO film[a)]

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Arsenic doped ZnO and ZnMgO films were deposited on SiO_2 using radio frequency magnetron sputtering and $ZnO–Zn_3As_2$ and $ZnO–Zn_3As_2–MgO$ targets, respectively. It was found that thermal activation is required to activate the formation of *p*-type conductivity. Hall measurements showed that *p*-type films with a hole concentration of $\sim 10^{17}$ cm^{-3} and mobility of ~ 8 $cm^2\ V^{-1}\ s^{-1}$ were obtained at substrate temperatures of 400–500 °C. The shallow acceptor formation mechanism was investigated using x-ray photoelectron spectroscopy, positron annihilation, low temperature photoluminescence, and nuclear reaction analysis. The authors suggest that the thermal annealing activates the formation of the As_{Zn}-$2V_{Zn}$ shallow acceptor complex and removes the compensating hydrogen center. © *2011 American Vacuum Society.* [DOI: 10.1116/1.3525639]

I. INTRODUCTION

Despite many efforts, *p*-type doping of ZnO still remains an important issue in ZnO-based device technology.[1] ZnO *p*-type doping is difficult, and the studies so far are not very reproducible and are controversial. There have been reports on the fabrication of arsenic doped *p*-type ZnO with hole concentrations ranging from 10^{16} to 10^{18} cm^{-3}.[2–7] Theoretical calculations showed that As_{Zn} is a donor and As_O is a deep acceptor (with ionization energy $E_i \sim 1000$ meV),[8] and thus, they would not be the shallow acceptor responsible for the *p*-type conduction. Using first principal calculations, Limpjumnong *et al.*[8] showed that As_{Zn}-$2V_{Zn}$ could be a relatively shallow acceptor having $E_i \sim 150$ meV for the (0/+) ionization, and its formation from its parent defects As_{Zn} and V_{Zn} was energetically favorable. Tentative assignment of this complex to the shallow acceptors in the As-doped *p*-type ZnO materials has thus been proposed.

In the present study, using the radio frequency magnetron sputtering method, we have fabricated As-doped *p*-type ZnO films on SiO_2 with a hole concentration ranging between $\sim 10^{17}$ and 10^{18} cm^{-3} and hole mobility of ~ 8 $cm^2\ V^{-1}\ s^{-1}$. We used x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), low temperature photoluminescence (PL), positron annihilation spectroscopy (PAS), and nuclear reaction analysis (NRA) to systematically investigate the shallow acceptor formation mechanism in As-doped *p*-type ZnO as well as the effects of thermal annealing.

II. EXPERIMENT

The ZnO films were fabricated using radio frequency magnetron sputtering at 10^{-3} Pa and using radio frequency power of 120 W. The films were deposited on to 250 nm thick SiO_2 grown on Si substrates thermally in dry oxygen. The As-doped ZnO films were grown by using a ceramic target containing Zn_3As_2 (molecular ratio of 1 mol %) and ZnO (molecular ratio of 99 mol %). The As-doped ZnMgO films were sputtered from a ceramic target containing ZnO, MgO, and Zn_3As_2, having the molecular ratios of 97.5 at. %,

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1.5 mol %, and 1.0 mol %, respectively. The substrate temperature during growth was varied as necessary.

The carrier concentrations of the samples at room temperature were obtained by Hall effect using the BioRad HL5500 system using the van der Waal's configuration. In order to investigate the reproducibility of the growth, the carrier types and concentrations with varying growing parameters for the As-doped ZnO samples (i.e., the substrate temperature) were obtained by averaging the measurements from samples produced from at least five independent growths. Details of the XRD, XPS, PL, and PAS measurements could be found in Ref. 7, and those of the NRA measurement were given in Ref. 9.

III. RESULTS AND DISCUSSION

Control samples fabricated by using a pure ceramic ZnO target (no arsenic) and similar growing parameters were grown using a substrate temperature of 450 °C. The control sample had electron concentrations of $\sim 6\times 10^{18}$ cm^{-3} and electron mobility of 17 cm^2 V s^{-1}. As-doped ZnO and ZnMgO samples were grown on the SiO_2 substrates with the substrate temperatures varying from 200 to 500 °C. XRD measurements were carried out to obtain the structural information on these samples. Single peaks at $\sim 2\theta = 34.35° - 34.52°$ (ZnO [002] direction) were observed in the XRD spectra of As-doped ZnO samples grown at substrate temperatures of 200, 400, and 450 °C, which implied that these conditions yielded films with single phase wurtzite structure with *c*-axis orientation. For the As-doped ZnO sample grown at 500 °C substrate temperature, other than the ZnO (002) peak, small peaks corresponding to ZnO (100) and ZnO (110) were also found. For the case of As-doped ZnMgO samples grown at all the substrate temperatures, single peaks at ~34.46° (ZnO [002] direction) were observed in the corresponding XRD spectra.

Secondary ion mass spectroscopy (SIMS) measurements were also carried out on the As-doped ZnO and ZnMgO samples grown at 450 °C. Arsenic was found to be uniformly present in both films, and uniform Mg distribution was observed in the ZnMgO film. The film thickness was ~280 nm. Calibrated with an As-implanted sample with known fluence, the As concentration in these films was $\sim 10^{19}$ cm^{-3}.

The carrier concentrations in the As-doped ZnO and ZnMgO samples are plotted against the growth temperature in Fig. 1. The samples were *n*-type at low growth temperatures and transited to *p*-type as the substrate temperature was increased. This trend was common to both ZnO and ZnMgO samples. This indicated that the formation of *p*-type conduction involves a thermal activation process. We have also performed a postgrowth annealing study in Ar on the As-doped ZnO sample grown at the substrate temperature of 200 °C, which was *n*-type prior to annealing. The sample was found to convert from *n*-type ($n=5\times 10^{16}$ cm^{-3}) to *p*-type ($p=2\times 10^{16}$ cm^{-3}) after the 400 °C postgrowth annealing. The hole concentration further increased to ($p=3\times 10^{16}$ cm^{-3}) as the annealing temperature was further increased to 500 °C.

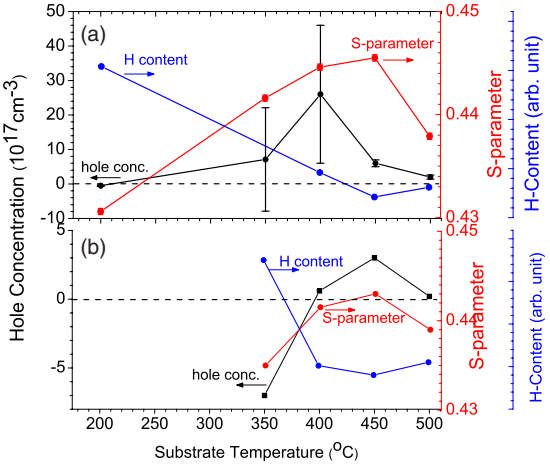

FIG. 1. (Color online) Hole concentration, *S*-parameter and hydrogen content as a function of the growth substrate temperature for (a) the As-doped ZnO sample and (b) the As-doped ZnMgO sample.

These results definitely confirmed that thermal activation is required for the formation of *p*-type conduction. It was noticed that a hole concentration of $10^{17}-10^{18}$ cm^{-3} and a hole mobility of 1–8 cm^2 V^{-1} s^{-1} were obtained for the As-doped samples grown at substrate temperatures of 400–450 °C.

The low temperature ($T=10$ K) near band edge PL spectra of the undoped ZnO, As-doped *n*-type ZnO (grown at substrate temperature of 200 °C), As-doped *p*-type ZnO, and ZnMgO (both grown at 450 °C of substrate temperature) are shown in Fig. 2. Three major peaks at 3.234, 3.308, and 3.355 eV were observed in the undoped ZnO sample PL spectrum. Emission lines with similar peak positions have also been observed from *n*-type ZnO prepared by sol-gel method[10] and from ZnO tetrapods.[11] These emissions at 3.234, 3.308, and 3.355 eV peaks are attributed respectively to the donor-acceptor-pair (DAP) emission, two-electron-satellite and/or exciton-LO phonon emission, and D_0X emission. Five major PL peaks were found in the As-doped *p*-type ZnO sample at 3.158, 3.197, 3.236, 3.282, and 3.337 eV. The 3.158, 3.197, and 3.236 eV were attributed to DAP

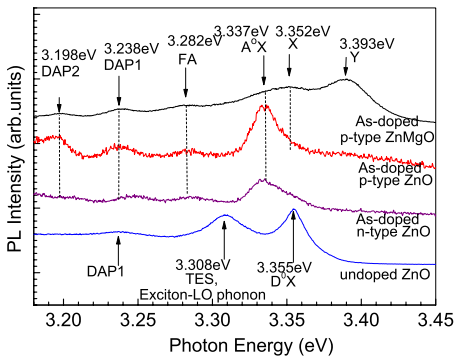

FIG. 2. (Color online) Near band edge PL spectra of the As-doped *p*-type ZnMgO (substrate temperature=450 °C), As-doped *p*-type ZnO (substrate temperature=450 °C), As-doped *n*-type ZnO (substrate temperature =200 °C), and the undoped ZnO samples measured at 10 K.

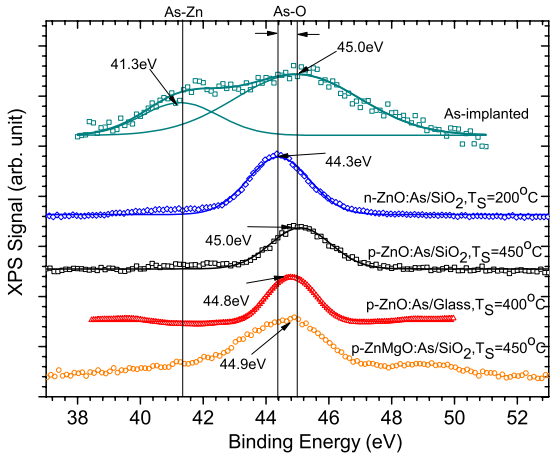

FIG. 3. (Color online) As 3*d* binding energy of the XPS spectra for the As-implanted sample and the different As-doped ZnO and ZnMgO samples.

emissions. The other two peaks at 3.282 and 3.337 eV were only observed in the *p*-type ZnO and ZnMgO samples and also in the *p*-type As-doped ZnMgO sample. They were attributed to free electron to acceptor (FA) emission and acceptor-bound exciton (A_0X) emission, respectively.[2,6,12] Taking the FA emission line energy $E_{FA}=3.282$ eV and $E_g=3.437$ eV,[13] the activation energy E_A of the corresponding acceptor can be calculated using $E_A=E_g-E_{FA}+kT/2$. This yields $E_A=155$ meV.

Figure 3 shows the As (3*d*) XPS spectra of the As-doped *n*-type sample grown at 200 °C, the As-doped *p*-type ZnO and ZnMgO samples both grown at 450 °C. A dominant peak at ~45 eV was found in all these As-doped samples. The binding energy of 45 eV is close to the previously reported value of the As–O bond,[14] and thus, this peak is attributed to the As atom substituting the Zn site (i.e., As_{Zn}) in the ZnO lattice. We have also carried out the XPS measurements on the as-As-implanted ZnO sample and on the As-implanted ZnO sample after the 750 °C postimplantation Ar annealing.[15] The implantation energy was 100 keV, which corresponded to an implantation depth extending to ~100 nm (obtained from TRIM calculation and SIMS measurement). We have attempted the As-implantation fluences of 10^{14} and 10^{15} cm^{-2}, which corresponded to As-concentrations of $\sim 10^{19}-10^{20}$ cm^{-3}. Despite successful fabrication of light emitting diodes operating at room temperature using the ion-implantation technique followed with postimplantation annealing,[16] no rectifying *IV*-behavior and thus no hint of *p*-type layer formation was observed in these As-implanted samples. The XPS spectrum of the as-As-implanted sample is also included in Fig. 3, and the XPS spectrum for the As-implanted sample annealed at 750 °C was similar. Two peaks ~41 and 45 eV were found. The 41 eV peak is attributed to the As–Zn bond[14] and thus was originated from the As_O defect site.

Using PAS as a selective probe sensitive to vacancy type defects, we investigated the Zn-vacancy related defects in the As-doped ZnO and ZnMgO samples grown at different substrate temperatures. PAS is based on the annihilation of incident positrons with electrons in the sample, and subsequent emission and detection of 511 keV gamma photons.[17,18] As a vacancy type defect presents as a potential well to the thermalized positron, the diffusing positron would be trapped by such open volume defects. The Doppler broadening of the 511 keV peak (parametrized by the *S*-parameter) is determined by the electronic environment in which the positron annihilates and thus the information about the corresponding vacancy state in the sample could be revealed. For the case of ZnO, only the Zn-vacancy related defects would trap positron but not the O-vacancy.[9] This implies that the variation of the observed *S*-parameter is a result of the change of the Zn-vacancy related defect. The increase of *S*-parameter corresponds with the increase of the open volume and/or the concentration of the relevant vacancy type defect. The *S*-parameters of the As-doped ZnO and ZnMgO samples as a function of growth substrate temperature are shown in Fig. 1. A strong correlation between the *S*-parameter and the rise of the hole concentration with increasing substrate temperature was observed in both types of samples. This implied an increase of the open volume and/or the concentration of the Zn-vacancy type defects in the ZnO and the ZnMgO samples while the substrate temperature was raised.

Figure 1 also shows the *H*-concentrations in the As-doped ZnO and ZnMgO samples as a function of the substrate temperature. *H*-concentrations were obtained using NRA. An anticorrelation between the *H* concentration and the hole concentration was clearly found in both types of sample.

PL-data showed that the shallow acceptor had an activation energy of $E_A=155$ meV, which was very close to the calculated ionization energy $E_i=150$ meV for the (0/+) ionization of the As_{Zn}-$2V_{Zn}$ acceptor complex. The XPS data showed that the majority of the As-atoms introduced into the films occupied the As_{Zn} site in the ZnO lattice, although it was not possible to distinguish whether the As_{Zn} structure involved was part of the As_{Zn}-$2V_{Zn}$ complex or it was the isolated As_{Zn}. From the experimental data, the formation of the *p*-type conductivity was associated with thermal excitation and was correlated with the increase of the *S*-parameter, i.e., the open volume and/or the concentration of the relevant Zn-vacancy related defects. Limpijumnong *et al.*[8] pointed out that for the shallow acceptor complex As_{Zn}-$2V_{Zn}$, the As–O bond adjacent to the V_{Zn} would be shortened by 5%.[8] This implied that the adjacent V_{Zn} would have a larger open volume. Thus, the observation of the increase of *S*-parameter is in agreement with the formation of the As_{Zn}-$2V_{Zn}$ complex. With these observations, we tentatively ascribe the observed *p*-type conductivity in our *p*-type As-doped ZnO and ZnMgO samples to the As_{Zn}-$2V_{Zn}$ complex.

It is also worth pointing out that the shallow acceptor related emission PL lines A_0X and *FX* were found in the As-doped ZnO sample fabricated at a low substrate temperature of 200 °C, although the sample was highly resistive but *n*-type conducting. This implied that some relevant shallow acceptors have already been formed and thus the resistive *n*-type conduction was probably due to the compensation by other defects. Our NRA data showed that hydrogen was gen-

erally present in all the As-doped ZnO and ZnMgO samples. Hydrogen impurity acting as donor would compensate the *p*-type conductivity. The *p*-type conductivity was thus enhanced with the thermal removal of the hydrogen compensating center as revealed by the NRA measurement.

IV. SUMMARY AND CONCLUSIONS

As-doped ZnO and ZnMgO films were grown on SiO_2 at different substrate temperatures. It was found that thermal activation was needed to introduce the *p*-type conduction in these films. The thermal process was probably associated with the formation of the As_{Zn}-$2V_{Zn}$ shallow acceptor complex and the removal of the compensating hydrogen impurity.

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