P-8-9

Structural, electrical characterization and sharp-blue electroluminescence of As-implanted bulk ZnO

J.D. Ye[1], L.J. Tang[1], S.F. Choy[1], C.H. Tung[1], S.T. Tan[1], X.W. Sun[1], G.Q. Lo[1], S. Tripathy[2], and K.L Teo[3]
[1]Institute of Microelectronics, A*STAR, Singapore 117685; yejd@ime.a-star.edu.sg; Phone: (65)-67705697 Fax: (65)-67731914
[2] Institute of Materials Research and Engineering, A*STAR, 3 Research Link Singapore 117602
[3] Electrical & Computer Engineering Department, National University of Singapore, Singapore 117576
and Data Storage Institute, A*STAR , Singapore 117608

1. INTRODUCTION

Ion implantation is a unique and attractive means of doping in a controlled manner in fabricating semiconductor materials and devices. Recently, research studies on ion-implanted ZnO were focused in converting n-type ZnO into p-type materials. However, few successes in p-type ZnO were achieved by ion implantation [1-3]. The ambiguity of doping mechanism hampers the production of reliable and reproducible p-type ZnO.

In this study, we are focusing on the failure mechanism investigation of p-type conversion in arsenic implanted bulk ZnO single crystal. The introduced damage buildup and lattice disorder were investigated and the electrical transport with depth-profiled defect atomic migration has been systematically revealed. The sharp blue electroluminescence emission around 430nm was attributed to the recombination of As-related donor-acceptor pair in implanted ZnO layer.

2. EXPERIMENTS

ZnO samples were hydrothermally grown (0001) single crystals. Implantation of arsenic (As) were performed 7° off the specimen normal with energy of 150 keV and the doses range from 2×10^{13} to 5×10^{15}cm^{-2}. After implantation, the post annealing were carried out in a wide temperature range of 500-1000°C for 2minutes or 2hours in oxygen ambient. The characterization means of SIMS, HRXRD, XTEM, Hall-effect, PL, Raman and EL measurements were carried out to reveal the structural, electrical, optical properties and related doping mechanisms.

3. RESULTS AND DISCUSS

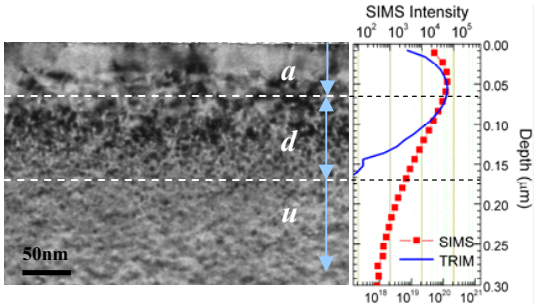

Fig.1 (left) Bright-field XTEM image and (right) SIMS and TRIM simulated depth-profile of As-implanted (8E14cm^{-2}) ZnO

Dopant Depth-profile Distribution The depth profile of the arsenic ions in ZnO implanted with dose of 8×10^{14}cm^{-2} has been measured by SIMS (right of **Fig.1**), which is well consistent with the simulation by TRIM program. Compared with the bright-field XTEM, three obvious regions were observed in Fig.1 (left): amorphous layer (*a*), damaged layer (*d*) and undamaged layer (*u*). After implantation, the displaced atom density in a surface layer "*a*" almost reaches the amorphous level, in which As ion concentration reaches maximum. A deeper damage band "*d*" with a high density of dislocations was also formed, extending to a depth of 170nm. The depth profile of TRIM simulation and XTEM damage distribution coincide exactly with each other.

Damage buildup and lattice disorder The HRXRD scans (2θ-ω) exhibits the increasing FWHM of ZnO (0002) diffraction peak. As dose increased, the diffraction signal from the damaged layer increased and separated to the undamaged layer (**Fig.2 (a)**). The low-angle shoulder is due to lattice swelling by interstitial atoms, while the high-angle shoulder is originated from the vacancies-induced lattice contraction [4]. After annealing, the separated shoulder gradually approached and almost merged into diffraction peak of undamaged layer, indicating the thermal recovery of lattice disorder and density reduction of interstitial defect (**Fig.2 (b)**). However, the enhancement of high-angle shoulder for 700°C annealing is ascribed to the merging of large-size vacancy clusters in the damaged layer, such as $(V_{Zn})_N$, which was dissociated again via high-annealing temperature.

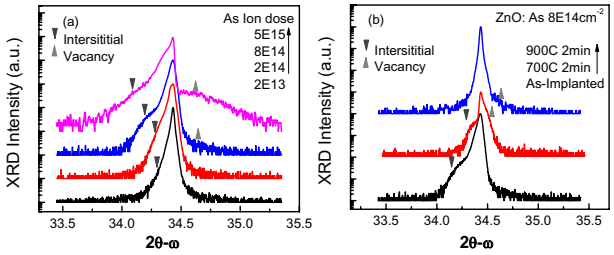

Fig.2 2θ-ω scans of implanted ZnO with different dose (a) and different post-annealing temperature.

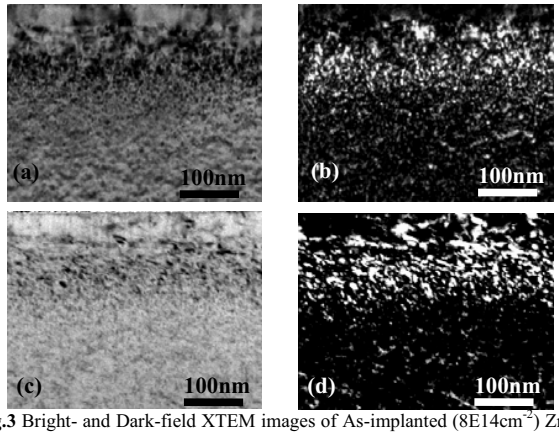

Fig.3 Bright- and Dark-field XTEM images of As-implanted (8E14cm^{-2}) ZnO. [(a) and (b) **g**=0002*, (c) and (d) **g**=2$\underline{1}$12*]

Fig.3 shows bright- and dark-filed (diffraction contrast) images of ZnO bombarded with 150keV As ions to dose of 8×10^{14} cm^{-2}. From viewing with **g** = 0002*, some point defect clusters were found to be formed [**see Fig.3 (a) and (b)**], while the coarse planar defects elongated to the basal plane of wurtzite structure of ZnO were seen in **g** = 2$\underline{1}$12* images [see **Fig.3 (c) and (d)**]. These observed defects were intestinal in nature and aggregate in the deep-damaged layer, in which the host interstitial defects such as Zn_i and O_i should be favorably formed [5]. The amorphous feature is also confirmed in the near-surface layer, where energetically favorable vacancy-related defect clusters are abundant and a result of stoichiometric imbalance with preferential loss of oxygen. These revealed defects clusters in different region determine the electrical transport and optical properties.

Electrical Transport and defect atomic migration After implantation, all samples were of n-type, with increasing concentration as the dose increased (**Table I**). The gradual reduction of electron mobility is ascribed to the scattering enhancement by arsenic impurity and implantation-induced host interstitial defects, and the partial crystal-to-amorphous transition. After annealing at moderate temperature (500-800°C) in oxygen ambient, the electron concentration increased greatly, as shown in **Table II**, however, the mobility is no obvious changes. The high temperature annealing over 900°C led to the great reduction of

electron concentration, even to high-resistance state for long-duration activation. The fail conversion of p-type to n-type is related to the amphoteric role of impurity Li in hydrothermally grown ZnO and atomic defect migration during annealing.

Table I. Hall data of implanted ZnO with different doses

	Undoped	As implanted with various dose (cm^{-2})			
		2×10^{13}	2×10^{14}	8×10^{14}	5×10^{15}
n ($\times10^{16}cm^{-3}$)	-16.6	-2.61	-3.24	-12.5	-215
μ (cm^2/V s)	168	101	127	51	1.45

Table II. Hall data of RTP annealed ZnO: As (8E14cm^{-2})

Duration		Post-activate annealing in oxygen ambient (^oC)					
		500	600	700	800	900	1000
2min	n ($\times10^{17}$ cm^{-3})	-	-47.7	-22.5	-25.4	-3.42	-2.14
	μ (cm^2/V s)	-	24.5	33.9	34.5	14.3	23.2
2hrs	n ($\times10^{17}$ cm^{-3})	-35.9	-49.8	-22.2	-89.5	HR	HR
	μ (cm^2/V s)	17.3	24.2	21	33.5	-	-

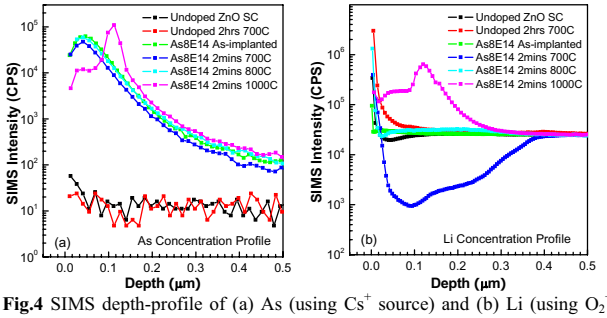

Fig.4 SIMS depth-profile of (a) As (using Cs^+ source) and (b) Li (using O_2^+ source) in undoped and implanted ZnO.

From SIMS results in **Fig.4 (a)**, no obvious changes were observed for As ion depth-profiled distribution in moderate annealing temperature, however, the concentration of Li ion in the damaged region varied greatly with the annealing temperature. For temperature up to 700^0C, the Li-lean region could be seen in **Fig.4 (b)**. This feature is due to the deactivation of Li by trapping of zinc vacancy clusters or oxygen interstitial defects [6]. The latter is more favorable due to the strong bond-effect of Li-O_i or formation of Li_2O inclusions [7]. In this case, the activated As dopants substitute to Zn site, As_{Zn}, acting as the shallow donor and resulting in the sharp increasing of electron concentration. As the annealing temperature increased over 900^0C, the vacancy clusters such as $(V_{Zn})_N$ were dissociated due to high thermal energy. The shallow donor Zn_i would return into the host lattice, and the deactivated O_i and Li_i would also be separated. It is noted that the depth-profile of As and Li is almost the same for 900^0C annealing, indicating that more As ions migrate from the near-surface amorphous layer to the deep-damaged layer, resulting in the possible formation of As_{Zn}-Li_i. In this case, the aggregation of Li in damaged layer, screen the formation of (As_{Zn}-nV_{Zn}) defect complex, which is proposed to be shallow acceptor for p-type conduction. It is summarized that the expected p-type conversion is not successful due to the Li blocking effect by Li-As formation and high-resistive damage layer with possible p-type was formed in the damaged layer beneath near surface region.

Lattice dynamic investigation of defects The defect revolution could also been verified by off-resonance Raman measurement. Compared to undoped bulk ZnO, the implanted ZnO show the great enhancement of E_1(LO) at ~580cm^{-1} and two anonymous modes "A" and "B" in **Fig.5**. The mode "A" at ~180cm^{-1} is assigned as the local vibration mode of Zn vacancy clusters, which increased in intensity with implantation dose. This mode was enhanced for 700^0C annealing and reduced after 900^0C annealing, confirming the revolution of the formation of large-size vacancy clusters and the dissociation and annihilation process with enough high thermal energy. The mode "B" at 565cm^{-1} exhibits the same trending with E_1(LO) mode, which both are actually the defect-intermediated resonant Frohlich characters [8]. The frequency differences are due to the different effective dielectric function of nano-voids or vacancy clusters formed within implanted layer. The revolution of modes "A" and "B" are well consistent with XRD and SIMS results.

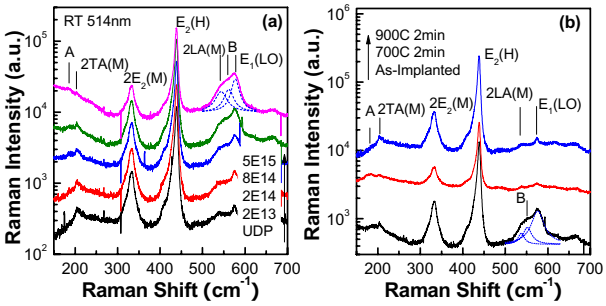

Fig.5 Off-resonance Raman spectra of ZnO samples (a) with different doses and (b) subjected to different annealing condition.

RT Photoluminescence and Electroluminescence With a forward bias applied, the sharp bright blue EL emission around 430nm with FWHM of 40nm was observed (**Fig. 6**). The coincidence of PL and EL spectra strongly suggests that origin of EL is mainly via the radiative recombination of deep acceptor-shallow donor pairs within the high-resitive/weak p-type conductive damaged layer. The possible candidate of deep-acceptor is the As_{Zn}-Li_i defect complex. The weak UV emission was due to the self-absorption effect/or field-induced exciton nonradiative annihilation. The deep level emission around 550nm was due to the intrinsic defects in ZnO. The high forward bias was due to the imperfect contacts to high-resistive implanted ZnO: As layer.

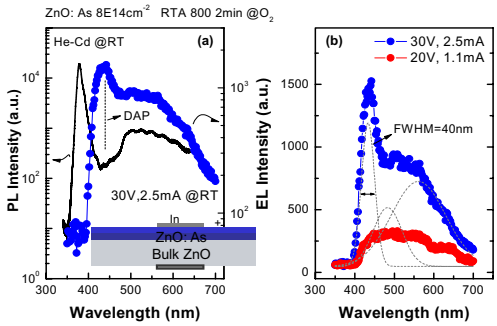

Fig.6 (a) Log-scale RT Photoluminescence (PL) and electroluminescence (EL) of As-implanted ZnO (RTA 800^0C for 2mins); **(b)** RT EL with different injection current.

4. CONCLUSION

The failure mechanism of p-type conversion in arsenic implanted in hydrothermally grown bulk ZnO have been systematically revealed via the investigation of depth-profile damage buildup, lattice disorder and defect migration process. High-resistive As-implanted ZnO layer was formed at high-activation temperature and the sharp blue electroluminescence emission around 430nm was observed, attributed to the recombination of As-related donor-acceptor pair in implanted ZnO layer.

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