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Codoping effects of the Zn acceptor on the structural characteristics and electrical properties of the Ge donor-doped GaN thin films and its hetero-junction diodes all made by reactive sputtering

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ABSTRACT

Zn acceptor/Ge donor (Zn/Ge)-codoped GaN films with different Zn contents have been deposited on Si substrates at 300 °C and at 90–150 W by RF reactive sputtering technique with cermet targets at the composition atomic ratios of Zn:Ge:(Ga + GaN) at x:0.03:(0.97-x) with x = 0, 0.03, 0.06, and 0.09 and Ga:GaN = 3:7. The films made with such targets were presented in an abbreviated symbol of Zn-x-GeGaN at x = 0, 0.03, 0.06, and 0.09. The morphology, structure, electrical properties, optical property, and hetero-junction diode devices involved in the Zn-x-GeGaN films were thoroughly investigated. The systematic Zn increment into the n-type Zn-0-GeGaN through property evaluation provides the supporting information in studying solid solutioning. Zn-x-GeGaN films converted into p-type semiconductor at x = 0.06 and 0.09. The values of bandgap were in the range of 2.87–3.17 eV with the lower value for the higher Zn content in Zn-x-GeGaN films. The higher RF power led to the faster growth, highly deficient in nitrogen, and a higher Zn atom ratio in the deposited film. The 120W-deposited Zn-0.06-GeGaN film had hole concentration of 7.21×10^{16} cm^{-3}, hole mobility of 39.1 cm^2 V^{-1} s^{-1}, and the electrical conductivity of 0.45 S/cm.

1. Introduction

GaN semiconductor material has the wide direct bandgap and interesting characteristics such as high breakdown voltage, high mobility, and thermal stability [1]. It has been realized that GaN and its alloys are employed in blue-light-emitting diodes (LEDs) and laser diodes (LDs) [2,3]. In 2014, Prof. S. Nakamura won the Nobel Prize for Physics and he showed that defect technology to control the electrical properties of GaN, which has been promising for the evolution of the p-type Mg-doped GaN in realizable the commercialization GaN-based LEDs. Alloy systems in GaN, Mg-GaN and In-GaN had been studied and the n-type doped properties were modified by efforts in Si-, Ge-, and Sn-doped GaN [4,5], while codoping GaN with Si donor and Zn acceptor was also reported [6,7]. Additionally, p-type GaN with high hole concentration becomes a key material for the improvement in photo-electronic and electronic devices [8–11]. However, fabrication of p-type doping is known to be hard for semiconductor with low valence-band maximum (VBM) energy, while it is difficult to obtain the high conduction-band minimum (CBM) energy in n-type doping by compensation and bipolar doping [12,13]. To overcome the drawback of p-type and n-type doping, the codoping technique has been used to effectively tune the dopant concentrations and properties of electronic and magnetic devices [14]. The codoping method can effectively increase the solubility of dopant and the rate of activation by an increment of the electrical mobility and the reduction of carrier ionization energy [15]. Katayama et al. [16] proposed the concept of codoping in which the donor and acceptor were doped at the same time to prepare p-type GaN with low resistivity. They doped Mg and Si into the lattice of GaN at a concentration of 2: 1. As a result, the acceptor energy level was decreased by codoping and the film was enhanced in the solid solubility of the dopant, electrical mobility, and carrier concentration. Besides, Kim et al. studied the doping Mg and Si in GaN by metalorganic chemical vapor deposition (MOCVD) in 1999. It was explained that the concept of competitive adsorption between Mg and Si during the deposition process to get the characteristics of Mg-Si codoping and to make p-GaN high electrical conductivity [17]. In 2000, Kim et al. [18] investigated the characteristics of Zn-Mg codoped GaN film deposited by metalorganic chemical vapor deposition technology. S. Nakamura et al. [19] mentioned that codoped Si and Zn in InGaN formed donor and deep acceptor energy levels, respectively. Sheu's research team [20] codoped Si and Zn atoms in InGaN by metal-organic vapor-phase epitaxy (MOVPE) in 2002 to form the donor and deep acceptor energy levels. In

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2012, M. A. Reshchikov et al. [7] measured the internal quantum efficiency (IQE) of codoped Si/Zn GaN films as high as 90% by using time-resolved photoluminescence (TRPL). They used the MOVPE method to grow n-type GaN: Si, Zn thin films on a sapphire substrate with a carrier concentration of (0.75–1.14) $\times 10^{19}$ cm^{-3} and carrier mobility of 150 cm^2 V^{-1} s^{-1} at room temperature.

In recent years, our group has successfully employed the RF reactive sputtering technique for the III-nitride compounds with single cermet targets to replace the pure Ga visco-liquid target [21–25]. The RF reactive sputtering technology provides an easy-accessible, easy-to-clean, and low-cost method and the targets used for this method have been designed in a wide range of the composition. Consequently, the study of acceptor/donor doping in semiconductors of III-nitride compound especially GaN can be easily executed. The sputtered *p*-type GaN and InGaN film had been achieved [21–23]. To study the effects of doping on the semiconductor properties, a systematic change in film composition is the basic strategy to study the solid solubility, the structure, properties, and their relationship for the purpose of understanding the possible defect nature.

In this work, we successfully grew Zn acceptor/Ge donor (Zn/Ge)-codoped GaN films on Si substrates by RF reactive sputtering technique with cermet targets at the metallic composition ratios of Zn:Ge:(Ga + GaN) = x:0.03:(0.97-x) with $x = 0$, 0.03, 0.06, and 0.09 and at Ga:GaN = 3:7. The targets were represented with the abbreviated symbol of Zn-x-GeGaN at $x = 0$, 0.03, 0.06, and 0.09, while its formed films were named as Zn-x-GeGaN films. The variation of the Zn content in Zn-x-GeGaN films can provide clear evidences for the study of the effect of point defects on film properties. The hetero-junction p-n diodes made with Zn-x-GeGaN films and *p*- or *n*-type Si substrates were also fabricated to evaluate the diode performance.

2. Experimental details

Zn/Ge-codoped GaN thin films were grown on Si substrates by RF reactive sputtering technology with a cermet target in the Ar and N_2 mixed atmosphere. The targets were made by hot pressing with the mixture of metallic Zn, Ga and Ge powders and ceramic GaN powder. After the cermet targets were fabricated by hot pressing at 300 °C for 1 h under argon, the corresponding films made with Zn-x-GeGaN targets were indicated as Zn-x-GeGaN films at $x = 0$, 0.03, 0.06 and 0.09. To avoid the oxygen and impurities, mechanical and diffusion pumps were employed to pump the chamber pressure down to 1×10^{-6} Torr before sputtering. To get rid of surface contamination of target from hot pressing, the first run with each target was the test run and used to clean the target surface with plasma for 1 h. During the formal depositing process, the substrate temperature was set at 300 °C and the gas admixture of Ar and N_2 flow was kept at a flow rate of 5 sccm and 15 sccm, respectively. The working pressure was fixed at 9×10^{-3} Torr while the RF sputtering power was 120 W and deposition time 30 min. The single cermet targets used in RF sputtering were 5.08 cm (2 in.) in the size and the working distance between target and substrates in chamber for sputtering was fixed at 5 cm. To study the influences of output RF power for sputtering on Zn-x-GeGaN films, the Zn-0.06-GeGaN target was used to to deposit films at sputtering power of 90–150 W. The choice of Zn-0.06-GeGaN target for films at different powers was based upon the performance data from the different Zn-x-GeGaN films at $x = 0$, 0.03, 0.06, and 0.09, with which the n-type → p-type conversion is expected to occur for the valuable p-type Zn-x-GeGaN.

The hetero-junction diode was also made by RF sputtering technique. The Zn-x-GeGaN films were deposited on the *n*-Si (100) or *p*-Si (100) substrates. The diodes owned the ohmic contact, as Al with low work function was selected for contact with the n-type layer (n-Si substrate or n-GaN based film) and Pt with the high work function was selected for contact with the p-type layer (p-Si substrate or p-GaN based film). The hetero-junction devices named device-A and device-B were made by the Zn-0-GeGaN and Zn-0.03-GeGaN films deposited on *p*-Si substrates, respectively. The *p*-Zn-GeGaN/*n*-Si hetero-junction diodes were fabricated by the Zn-0.06-GeGaN and Zn-0.09-GeGaN films grown on *n*-Si substrates to form device-C and device-D, respectively. Those above-mentioned diodes were deposited on Si wafer with the "top-top" electrode designing. The n-Si (100) wafer with polished surface had sheet resistance of ~ 1–10 Ω cm, thickness of ~ 550 µm, the carrier concentration of $\sim 10^{15}$ cm^{-3}, and mobility of ~ 200 cm^2/V s. Besides, the boron-doped p-Si(100) wafer had a flat surface, the sheet resistance of ~ 1–10 Ω cm, the thickness of ~ 650 µm. Pt and Al metals were, respectively, used to make Ohmic contacts with the *p*- and *n*-type semiconductors for diodes. The electrodes were deposited at 200 °C for 30 min with the pure Al and Pt targets (99.999%) on the tops of film. The detailed processes for making the diodes with our sputtered III-nitride films were mentioned in our previous work [10,21,24,26,27].

X–ray diffractometry (XRD, D8 Discover, Bruker) and high–-resolution transmission electron microscopy (HRTEM, Technai G2, Philips) were employed to study the structure of crystalline Zn-x-GeGaN films. The morphology of surface and cross-section images of the Zn-x-GeGaN films were observed by scanning electron microscopy (SEM, JSM-6500F, JEOL). Atomic force microscopy (AFM, Dimension Icon, Bruker) was used to determine the topography of surface and the root-mean-square (*rms*) values of roughness of these films. The compositional analyses of Zn-x-GeGaN films were proceeded by the energy dispersive spectrometer (EDS, JSM-6500F, JEOL) on SEM. Hall measurement system (HMS-2000, Ecopia) with a maximum magnetic field of 0.51 T was applied to measure the electrical concentration, electrical conductivity and mobility of Zn-x-GeGaN films, while their absorption spectra were tested by ultraviolet-visible (UV–Vis) spectrometer (V-670, Jasco) The electrical properties of the diodes were investigated by the I-V tests with a Semiconductor Device Analyzer (Agilent, B1500A) at room temperature.

3. Results and discussions

3.1. Influences of Zn dopant content on structural and properties of the sputtered Zn-x-GeGaN films

Table 1 shows the EDS composition analyses of Zn-x-GeGaN films with different Zn contents ($x = 0$, 0.03, 0.06 and 0.09) grown at 120 W in power and the temperature of 300 °C under Ar and N_2 flow of gases. The [N]/([Zn] + [Ga] + [Ge]) atomic ratios were 0.938, 0.909, 0.876 and 0.865 for Zn-x-GeGaN films at $x = 0$, 0.03, 0.06, and 0.09, respectively and the nitrogen composition appeared to be lower at the higher Zn content. The [Zn]/([Zn] + [Ga] + [Ge]) atomic ratios were 0, 0.047, 0.079, and 0.129, as the Zn cationic contents in cermet targets were 0, 3, 6 and 9 at%, respectively. From EDS testing data, the Zn contents in Zn-x-GeGaN films were noticeably higher than those in the targets. It is expected that there was a higher sputtering yield for Zn than other composition like Ga and GaN. Besides, the data in Table 1 also shows that the [Ge]/([Zn] + [Ga] + [Ge]) atomic ratios were 0.042, 0.036, 0.037, and 0.041 for Zn-x-GeGaN at $x = 0$, 0.03, 0.06, and 0.09, respectively and Ge content in films was slightly higher the expected Ge ratios of 3 at% in the sputtered targets. The basic trend in Table 1 is that the higher Zn doping content leads to the higher Zn amount and the much nitrogen deficiency or the more nitrogen vacancies in film. As the concentration of cationic Zn becomes higher, the total cation charge becomes lower. In order to have charge balance, the N content needs to be lower at the same time.

Fig. 1a presents the XRD patterns of the Zn-x-GeGaN films ($x = 0$, 0.03, 0.06, and 0.09) deposited by RF sputtering at power of 120 W. From the XRD investigation, all Zn-x-GeGaN films sputtered on Si substrates had a wurtzite crystal structure. The diffraction $(10\bar{1}0)$, $(10\bar{1}1)$ and $(11\bar{2}0)$ peaks were distinctly detected from these Zn-x-GeGaN films with the preferential $(10\bar{1}0)$ growth plane without second phases being found. The diffraction intensity of $(10\bar{1}0)$ peak became weaker and that