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Electrical and structural characteristics of Ge-doped GaN thin films and its hetero-junction diode made all by RF reactive sputtering

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ABSTRACT

The Ge-*x*-GaN thin films were grown on Si (100) substrates by RF reactive sputtering technology with single cermet targets at the Ge/(Ge + Ga) molar ratios of $x = 0$, 0.03, 0.07 and 1. The Ge-*x*-GaN films had a wurtzite structure with a preferential $(10\bar{1}0)$ plane. The SEM images showed that Ge-GaN films were smooth, continuous, free from cracks and holes, and possessed grains in nanometer-size. All Ge-*x*-GaN films remained as n-type. While the highest conductivity was found to be $1.46\ S\ cm^{-1}$ in Ge-0.03-GaN film due to the highest carrier concentration of $2.55 \times 10^{18}\ cm^{-3}$. Additionally, we made the *n/p* diodes with Ge-doped GaN films as n-type layers deposited on Si (100) substrate as p-type layer using by RF reactive sputtering technique. Their electronics characteristics were evaluated in terms of the barrier height, ideality factor, and series resistance.

1. Introduction

Nitride compound semiconductors such as GaN, AlN, InN and their alloys have been the excellent materials for electronic and opto-electronics applications. With the promising characteristics such as wide direct band gap, high electrical conductivity and the commercialized growth process [1,2], GaN and its alloys have been applied for electronic devices such as metal-oxide-semiconductor field-effect transistor (MOSFET), hetero-junction field-effect transistor (HJ-FET), Schottky diode, p-n junction diode, and photo-electronic devices such as laser diode and light emitting diode [3–8].

Forming the n-type semiconductor materials from doping, the first principles calculation was studied by Van de Walle group and they found that while donors are readily formed with Si and O, nitrogen vacancies are difficult to form [9]. It is main reason that the properties of oxygen support it cause of unintentional n-type conductivity. Besides, compared with the efficiency of doping of Ge, Shuji et al. found that the efficiency of doping Si was higher as the GeH_4 and SiH_4 precursors were employed for Ge- and Si-doped GaN with high electronic concentrations at $2 \times 10^{19}\ cm^{-3}$ and $1 \times 10^{19}\ cm^{-3}$, respectively [10]. By using AlN buffer layer and metalorganic vapor phase epitaxial (MOVPE) method, Hiroshi et al. reported that both Si-doped GaN and $Al_{0.1}Ga_{0.9}N$ films fabricated on sapphire substrates had the electrical conductivities controllable by adjusting the SiH_4 flow rate and the Si-doped $Al_{0.1}Ga_{0.9}N$ film had high-quality crystal structure and good morphology of surface [11]. Furthermore, S.I. Molina et al. used MBE process to fabricate Si-doped GaN films on Si substrate. They investigated Si dopant level of the GaN film and they determined that the density of planar defect in the fabricated GaN film dramatically rose with the level of Si dopant [12]. The first principles calculations were employed to characterize the electronic properties of Si and Sn-doped GaN by Qinan et al. and they proved that Si and Sn operated as shallow donors in GaN and co-doping of Si and Sn in GaN caused the lower strain or lattice distortion and higher electron mobility [13]. To study the optical properties of Ge donor ionization energy, Shikanai et al. prepared Ge-doped GaN films by MOCVD method [14]. Additionally, Si in GaN and InN and Ge in InN were extremely fixed at the cation site in the core of the nanowires to present n-type semiconductor properties [15]. Ge worked as a donor in GaN film was prepared by plasma-assisted molecular beam epitaxy (MBE) process [15,16].

The Ge-doped GaN layers have been fabricated by different deposition technologies. These technologies have been given as hydride vapor phase epitaxy (HVPE) [17], chemical vapor deposition, MOCVD [10,18,19], metalorganic vapor phase epitaxy (MOVPE) [20,21], MBE [15], and thermionic-vacuum arc [22]. However, there was not any report for the electrical properties of the Ge-doped GaN film grown by using reactive sputtering technology until this work. In recent years, our group has successfully used the reactive sputtering technique for the IIInitride compounds with single cermet targets instead of using pure Ga liquid target [23–27]. The reactive sputtering has the promising characteristics such as it is much cheaper and easy to clean and its design on target can cover the composition in a wide range, therefore the research of doping in III nitride compound semiconductors especially GaN has been easily performed. The sputtered p-type GaN and

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InGaN film had been achieved [23–25]. To study the effects of doping on the semiconductor properties, the basic condition for executing investigation is the solubility of dopant in GaN.

In this work, we successfully fabricated Ge-x-GaN thin films (x = 0, 0.03, 0.07, and 0.1) on Si (100) substrates by RF reactive sputtering technique with single cermet targets. Using the RF sputtering technology, the p-n diodes were made by combining the n-type Ge-GaN films and the p-Si substrates. From this work, we can indicate the advantages of the RF reactive sputtering technique involved in the low depositing temperature, cheap equipment, safe and environmentally working in fabricating the Ge-doped GaN films.

2. Experimental details

Ge-doped GaN films deposited on Si (100) substrates were fabricated by using radio-frequency (RF) reactive sputtering with the (Ge + Ga + GaN) cermet targets. The names of Ge-*x*-GaN films with *x* = 0, 0.03, 0.07, and 0.1 were used to express the films made of four kinds of cermet targets with the Ge/(Ge + Ga) molar contents of 0, 0.03, 0.07, and 0.1 at%, respectively. The cermet targets composed of different Ge contents were made by hot pressing the mixture powder of ceramic GaN and metallic Ge and Ga in agreement with the design of composition. Before sputtering, the mechanical and diffusion pumps were used to pump down the chamber pressure to lower than 1×10^{-6} torr. For depositing Ge-doped GaN films, the sputtering power and substrate temperature were kept at 120 W and 300 °C, respectively. The deposition was proceeded for 30 min under the gas mixture of Ar and N_2 at the flow rates of 5 sccm and 15 sccm for each. To ensure the nitrogen in GaN being sufficient, the strategy of a larger amount of N_2 gas input was executed. For the hetero-junction diode, the Ge-*x*-GaN films were sputtered on the p-Si (100) substrate. Using the commercially available metal Al and Pt targets, the diodes had ohmic contacts fabricated by RF sputtering technique. The detailed procedures for preparing the diodes with our sputtered III-nitride films can be referred to our previous work [7,8,23,26].

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

3. Results and discussion

Table 1 shows EDS compositional analyses of the Ge-*x*-GaN films at *x* = 0, 0.03, 0.07, and 0.1. The [Ge]/([Ge] + [Ga]) molar ratios were 0, 0.042, 0.085, and 0.111 for Ge-*x*-GaN films at *x* = 0, 0.03, 0.07, and 0.1, respectively. The Ge molar ratio in the grown Ge-*x*-GaN film was slightly higher than that in the target. All compositions of nitrogen in the Ge-*x*-GaN films were between 48.4% and 49.4% or the [N]/([Ga] + [Ge]) ratios were in the range of 0.94–0.98, which determined that the Ge-*x*-GaN films were in a slight nitrogen-deficient state and had a close amount of nitrogen vacancies to equally contribute to their electrical properties. It is our expectation that the Ge content in deposited film can have strong effects on film properties including crystalline structure, surface morphology, electrical properties, and the energy bandgap.

Table 1
Compositional analyses of Ge-*x*-GaN films at *x* = 0, 0.03, 0.07, and 0.1.

x Ge-*x*-GaN	Ga (at%)	Ge (at%)	N (at%)	[Ge] / ([Ga] + [Ge])	[N] / ([Ga] + [Ge])
0	50.56	–	49.44	–	0.978
0.03	49.45	2.16	48.39	0.042	0.938
0.07	46.83	4.35	48.82	0.085	0.954
0.1	45.27	5.66	49.08	0.111	0.964

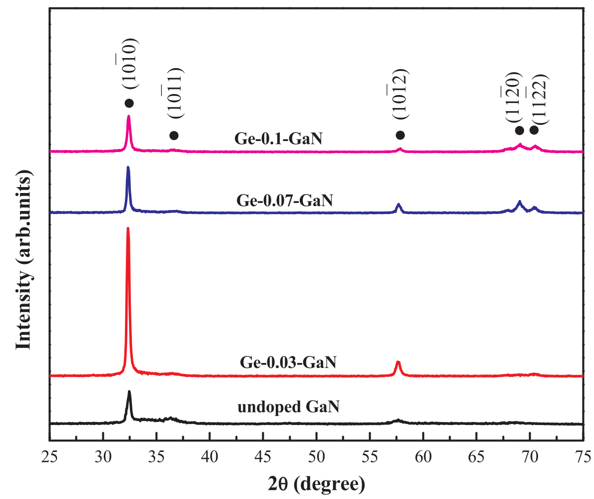

Fig. 1. XRD patterns of Ge-*x*-GaN films deposited at 300 °C and 120 W RF power in Ar/N_2 atmosphere with different Ge contents in cermet targets (*x* = 0, 0.03, 0.07, and 0.1).

The XRD spectra of the Ge-*x*-GaN films (*x* = 0, 0.03, 0.07, and 0.1) deposited by RF reactive sputtering at 300 °C and 120 W under the Ar/N_2 gas atmosphere are presented in Fig. 1. From the XRD data, all Ge-*x*-GaN films grown on Si (100) substrates had a structure of wurtzite. The (10$\bar{1}$0), (10$\bar{1}$1), (11$\bar{2}$0) and (11$\bar{2}$2) peaks were clearly observed from these Ge-*x*-GaN films with a preferential (10$\bar{1}$0) growth plane and there were no other second phases discovered. The intensity of the (10$\bar{1}$0) plane from the Ge-*0.03*-GaN film became highest. However, the intensity of this peak became weaker and the film had poor crystallinity as Ge content in sputtered films increased. The (10$\bar{1}$0) peak also slightly shifted to a higher 2θ angle at the higher Ge content, from 32.35° for Ge-*0.03*-GaN film to 32.40° for Ge-*0.1*-GaN film. All the considered data from the XRD measurement is listed in Table 2. It is shown that lattice constants of *a*, *c* and the volume of unit cell of Ge-*x*–GaN films decreased as Ge content in the grown films increased. While the lattice constant of *c* was 5.09 Å for undoped-GaN and was 5.54 Å for Ge-0.03-GaN, this constant dropped to 5.49 and 5.29 Å for Ge-0.07-GaN and Ge-0.1-GaN film, respectively. Besides, *a* was 3.13 Å for Ge-0-GaN and 3.41 Å for Ge-0.03-GaN, but declined to 3.38 Å for Ge-0.07-GaN and 3.25 Å for Ge-0.1-GaN. Additionally, cell volumes of Ge-*x*-GaN films at *x* = 0, 0.03, 0.07 and 0.1 was 43.14, 55.59, 54.26 and 48.38 at $Å^3$, respectively. From the value of 2θ degree, there was a slight decrease in the full width at half maxima (FWHM) values of the (10$\bar{1}$0) peaks from

Table 2
Structure properties of Ge-*x*-GaN thin films (*x* = 0, 0.03, 0.07, and 0.1) from the X-ray diffraction analyses.

x Ge-*x*-GaN	2θ (10$\bar{1}$0) peak	*a* (Å)	*c*(Å)	*Volume* ($Å^3$)	FWHM (10$\bar{1}$0) (deg.)
0	32.44	3.13	5.09	43.14	0.31
0.03	32.35	3.41	5.54	55.59	0.26
0.07	32.36	3.38	5.49	54.26	0.27
0.1	32.40	3.25	5.29	48.38	0.27