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Properties optimization with high nitrogen content doping for InGaZnO films deposited by reactive sputtering with a GaN-embedded cermet target

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ABSTRACT

GaN-embedded cermet target is used in this work for reactive sputtering to deposit the nitrogen-doped indium gallium zinc oxide (N-IGZO) films at different plasma atmospheres and to understand the heavily nitrogen doping in IGZO films for the possible application of IGZO thin film transistor (TFT) in the near future. Materials properties of N-IGZO films in crystallinity, microstructure, and electrical and optical properties were systematically investigated. The experiment showed that IGZO films with the high [N]/([O] + [N]) ratios of 0.11–0.14 showed low surface roughness of 0.26–0.43 nm, low carrier concentration of 2.36×10^{15}–2.16×10^{16} cm^{-3}, high mobility of 23–46 $cm^2/V\,s$, suitable electrical conductivity of 0.0143–0.157 $S\,cm^{-1}$, wide band gap of 3.32–3.47 eV, and high transparency of 85–89%. This is a pioneer work in IGZO film with a high nitrogen content above 10% at the anion site.

1. Introduction

IGZO TFT has been the key component of the transparent and flexible displays for consumable and industrial electronic devices due to its good electron mobility, high optical transparency, and low process temperature [1,2]. However, IGZO TFT has the degradation problems in the field-effect mobility, off-current, and the $I_{on/off}$ ratio due to the unstable interaction between the environmental atmosphere and the existing oxygen vacancies [3–6]. Different approaches have been applied to solve the degradation problems such as the higher N_2 pressure annealing [7], passivation layer deposition [8], and element doping [9–12].

Nitrogen doping has been widely recognized as the solution to stabilize the IGZO film properties [13–15] by decreasing the defects in the insulator/channel interface and channel to avoid the adverse effect of ambient atmosphere [15,16]. Nitrogen plasma treatment had suppressed the temperature instability in InGaZnO TFTs with the nitrogen doping [13,17,18]. However, the N content in IGZO after the N_2 plasma treatment was only in the range of 0–3.05%. Its carrier concentration decreased from 1.87×10^{19} to 6.64×10^{16} cm^{-3} after the nitrogen doping, while keeping Hall mobility at 7–10 $cm^2/V\,s$ [13]. The nitrogen content doped in IGZO after low temperature RF sputtering with an IGZO target (In_2O_3:Ga_2O_3:ZnO = 1:1:1 mol%) under the N_2-existing plasma has been limited due to the difficulty in converting the metal-O bonding into the metal-N bonding. As the N contents doped in IGZO from all the reported data are limited, its optimal N content for the good performance of TFT might not be achieved yet.

The industrial application of IGZO thin film has focused on TFT device performance, so a standard all-oxide sintered target containing In_2O_3:Ga_2O_3:ZnO = 1:1:1 has been commercially available. For the research study, the targets for IGZO films have been made by sintering the mixed oxide powders in different oxide ratios. However, the vacuum sputtering deposition of oxides under vacuum can lead to the oxygen vacancies inside the films to degrade its long-term electrical stability, especially for films grown at higher deposition temperature of 400 °C [19]. Without a new design for the IGZO target, the incorporated N content in IGZO films could not be explored to its limit.

The N-containing GaN compound embedded in a sputtering cermet target is proposed in this work for incorporating nitrogen into IGZO film. Considering the feasible target preparation in our laboratory, a cermet target containing metals of In and Zn and ceramics of In_2O_3 and GaN has been designed and prepared by low temperature hot pressing below 200 °C. By adjusting the N_2 input flow for the easy nitridation of metals and the O_2 flow for the easy oxidation of metals, the optimal [N]/([O] + [N]) ratio between 0 and 0.25 in IGZO films for a good transparent semiconductor for transistor can be evaluated. Up to present, it is rare to have reports discussing the N-IGZO semiconductor film with the [N]/([O] + [N]) ratio above 0.1, while keeping the high optical transparency, low carrier concentration, and good electron mobility.

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2. Experimental details

Nitrogen-doped IGZO thin films on SiO_2/Si and quartz substrates were prepared by radio-frequency (RF) reactive sputtering at 400 °C with single ($In + Zn + In_2O_3 + GaN$) cermet target under the O_2/N_2/Ar atmosphere with the N_2, O_2, and Ar flow rates of x, (10-x), and 10 sccm, respectively, whereas the x values are 0, 2.5, 3.7, 5, and 10. The IGZO films prepared at different x values for adjusting the N/O ratio were abbreviated as N-x-IGZO with x = 0, 2.5, 3.7, 5, and 10. The cermet target with 45 at% In, 10 at% Zn, 10 at% In_2O_3, and 35 at% GaN was fabricated by hot pressing the powder mixture of In, Zn, In_2O_3, and GaN at 170 °C for 30 min under vacuum. During the deposition, the chamber pressure was pumped down to 1×10^{-6} Torr by diffusion pump before sputtering, while 9×10^{-3} Torr during sputtering under the mixed gas atmosphere.

X–ray diffractometry (XRD, D8 Discover, Bruker) and high–-resolution transmission electron microscopy (HR-TEM, Tecnai G2, Philips) have been used to study the crystal structure of N-x-IGZO films. Scanning electron microscopy (SEM, JSM–6500F, JEOL) and atomic force microscopy (AFM, Dimension Icon, Bruker) were employed to analyze the surface morphology and topography of N-x-IGZO films. Compositional analyses of these films were conducted by the energy dispersive spectrometer (EDS, JSM–6500F, JEOL) provided on SEM. The element mapping of catalysts was performed by scanning transmission electron microscopy (STEM, Tecnai G2 F20, Philips). A Hall measurement system (HMS–2000, Ecopia) with a maximum magnetic field of 0.51 T was used to measure electrical properties. Ultraviolet–Visible (UV–vis) spectrometer (V–670, Jasco) was used for the absorption spectra. Spectroscopic ellipsometer (Woollam M-2000VI) was applied for measuring the refractive index as a function of optical wavelength.

3. Results and discussion

Composition data of the N-x-IGZO films deposited at 400 °C with a cermet target at x = 0, 5, 6.3, 7.5, and 10 obtained by the EDS system attached on SEM are analyzed, summarized, and showed in Table 1. Under the sputtering condition of 120 W and 400 °C, the films consistently increased the [N]/([N] + [O]) content from 0.11 at x = 0 to 0.26 at x = 10. Even sputtering at the N_2-free or x = 0 condition, the IGZO film contained 11% nitrogen at the anion sites, which had been favored to replace the oxygen vacancies and stabilize the film electrical properties. For the metal composition, N-0-IGZO had much higher Zn content and lower In and Ga contents than others. N-x-IGZO films at x = 5, 6.3, 7.5, and 10 had 59–64% In, 25–27% Ga, and 10–15% Zn, as compared with 51% In, 20% Ga, and 28% Zn for N-0-IGZO, respectively. It is apparent that the Zn atoms bombarded out of the target by the Ar-generated plasma, compared with In, In-O, and Ga-N molecules, are preferentially oxidized to lead to the high Zn content in film, as the ($In + Zn + In_2O_3 + GaN$) target was sputtered under the (O_2 + Ar) atmosphere. At the (N_2 + Ar) atmosphere with x = 10, the film was oxidized with the O atom from In-O in target bombarded out of target and slightly favored to from the In-N bonds than the Zn-N bond, as considering the increased In content at higher the N_2 flow rate. Therefore, the N-10-IGZO film had a lower Zn content. At the ($N_2 + O_2$ + Ar) atmosphere with $x \geq 5$, the nitridation involved in the film growth reaction and the N content started to quickly increase. As evidenced by an abrupt increase in the N content from 17% to 26% for IGZO films grown at higher N_2 flow rates increasing from 7.5 sccm to 10 sccm, the nitridation was much favorable at the atmosphere with a high N content, where metal components could be easily oxidized. For the films grown at the atmosphere with a low N content, the N ratio in films only increased from 11% to 14%, as the $[O_2]/([N_2] + [O_2])$ ratio of flow rate for reaction gases changing from 1 at x = 0 to 0.37 at x = 6.3. Therefore, the nitridation was much difficult at the atmosphere with a high O content. It is a strong contrast if we compare with the N-0-IGZO film to have 11% nitrogen at the anion sites just by adding GaN component in sputter target. It has been difficult from literature reports to have a higher N content in IGZO films deposited with a ($In_2O_3 + Ga_2O_3$ + ZnO) target. This work has provided an approach to have IGZO film with the N content larger than 10% at the anion site.

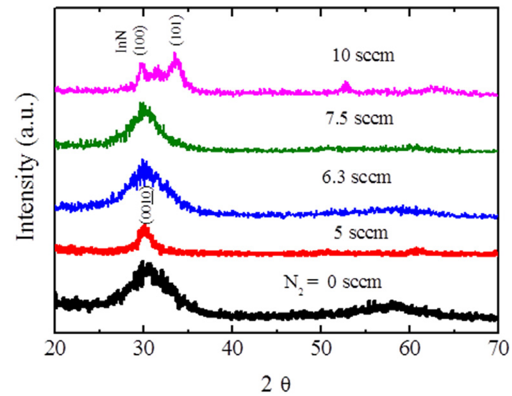

Fig. 1. XRD pattern of the N-x-IGZO films deposited at different N_2 flow rates.

Fig. 1 shows XRD patterns of the N-x-IGZO films deposited with a cermet target at different N_2 flow rates. Except for N-10-IGZO, all films showed an extremely broad peak at $2\theta \sim 30.3°$, which was contributed from the (00$\underline{10}$) preferential growth plane of a dihexagonal dipyramidal structure, referring to PDS No. 38-1097 for the $In_2Ga_2ZnO_7$ phase. Their full-width-half-maximum (FWHM) values of the (00$\underline{10}$) peak were in the range of 2.71–2.91°. Based upon the Scherrer's equation of $D = K\lambda/\beta\cos\theta$, where D is the crystallite size, K a constant of 0.9, λ the x-ray wavelength, and θ the diffraction angle, the corresponding crystallite sizes were in the range of 2.8–3.2 nm, which is related to the nano-crystallinity in the N-x-IGZO films. For the N-10-IGZO film, the InN phase of PDF No. 79-0621 with the dihexagonal dipyramidal structure occurred together. The InN peaks belonged to (100) at 33.7° and (101) at 33.7°, shifting to the higher angle due to the solid solutioning of the smaller ions of Ga^{3+} and Zn^{2+} to replace In^{3+}. The nano-crystalline size of N-10-IGZO film was much larger at 8.3 nm.

Fig. 2 shows (a–e) SEM cross-sectional images and (f-j) the 3D AFM morphologies of the N-x-IGZO films deposited at different N_2 flow rates. Due to the fine crystallinity size, only SEM cross-sectional images and 3D AFM images were shown. The film/substrate interface did not show

Table 1
Compositions of IGZNO films sputter deposited with a cermet target at the N_2, O_2, and Ar flow rates of x, (10-x), and 10 sccm.

x	at% in total | ratio in total cations						at% in total | ratio in total anions			
	In		Ga		Zn		N		O	
0	15.07	0.51	6.13	0.20	8.16	0.28	7.55	0.11	63.09	0.89
5	20.55	0.59	9.26	0.26	5.08	0.15	8.7	0.13	56.42	0.87
6.3	19.51	0.61	8.81	0.27	3.52	0.12	9.29	0.14	58.87	0.86
7.5	21.46	0.60	9.03	0.25	5.27	0.15	10.64	0.17	53.60	0.83
10	21.76	0.64	9.33	0.26	3.42	0.10	17.03	0.26	48.45	0.74