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Effects of annealing temperature on the carrier concentrations, the carrier mobilities and the quality of nitrogen doped ZnO films deposited by magnetron sputtering

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ZnO is a very promising *n*-type semiconductor with a wide band gap of 3.3 eV. It is one of a few materials which can be utilized to make optical devices emitting light in short wave length region [1]. ZnO has a potential of higher efficiency in emitting short wave length laser than GaN since the exciton binding energy of ZnO (60 meV) is larger than that of GaN (28 meV) [2]. Recently many techniques have been used to grow epitaxial ZnO films which will be used to fabricate optoelectronic devices. These techniques include molecular beam epitaxy (MBE) [3], pulsed laser deposition (PLD) [4], molecular organic chemical vapor deposition (MOCVD) [5], sputtering [6], reactive thermal evaporation [7], sol-gel process [8], ion beam deposition [9], spray prolysis [10], zinc oxidation [11], electrodeposition [12], atomic layer epitaxy (ALE) [13]. Among these techniques sputtering may be the most commonly used technique because it is possible to obtain high quality epitaxial films easily. One of the obstacles in realizing optoelectronic devices based on ZnO is the fabrication of *p*-type ZnO because all the as-grown ZnO films without doping show *n*-type characteristics [14]. High level *p*-type doping is necessary to overcome the background self-compensation effect of the intrinsic *n*-type defects such as oxygen vacancies and zinc interstitials [14], but the problem is that the solubilities of most elements in ZnO for *p*-type doping are not high enough. Nitrogen is one of the most promising candidates for the p-type dopant for ZnO [15]. Kawai *et al.* [16] reported that N_2O plasma is more efficient than NH_3 or N_2 plasma in doping nitrogen as a *p*-type dopant.

In this communication we report the effects of the flow ratio of N_2O/Ar in ZnO sputtering and the substrate temperature in post-annealing on the quality of the ZnO film and the carrier concentration and the carrier mobility in the ZnO film. Understanding these effects would give us an insight on how to obtain *p*-type ZnO effectively.

ZnO films were deposited on single crystal-sapphire substrates by rf-magnetron sputtering using a ZnO target. The sputter chamber was pumped down to 10^{-7} Torr using rotary and turbomolecular pumps before introducing Ar and N_2O gas into the chamber. In this study N_2O gas was used to dope nitrogen into ZnO thin films as a *p*-type dopant. The flow rates of Ar and N_2O gas were controlled by mass flow controllers. The N_2O flow rate was 5, 10, or 15 sccm, but the Ar flow rate was fixed at 30 sccm. ZnO film deposition was performed at room temperature under a fixed pressure of 0.05 Torr. N_2O gas was changed to N_2O plasma and Ar to Ar ion or Ar plasma in the chamber prior to ZnO sputtering. After ZnO deposition the samples were annealed in oxygen atmosphere in vacuum annealing furnace at 600, 800, or 1000 °C for 1 h. X-ray diffraction analyses were performed using Cu K_α radiation to investigate the crystal quality of the ZnO films. Hall measurements were made to investigate carrier concentrations and carrier mobilities in ZnO films. The electrical resistivities of the samples were measured using a four point probe.

Fig. 1a and b are the X-ray diffraction (XRD) spectra for the ZnO thin films deposited on sapphire substrates by magnetron sputtering and then annealed at 1000 °C in oxygen atmosphere for 1 h. The XRD patterns indicate that the as-deposited and then annealed ZnO thin films are monocrystalline or polycrystalline with a highly *c*-axis oriented texture. It was revealed by SEM observation that the ZnO films are polycrystalline. The full width at half maximum (FWHM) of the ZnO (002) diffraction intensity in the XRD spectra are shown in Fig. 2 as a function of annealing temperature for different N_2O/Ar flow ratios. The FWHM of a diffraction peak in XRD spectra is one of the measures widely accepted for crystal quality assessment. Smaller FWHM indicates better crystal quality. Fig. 2 tells us that regardless of the N_2O/Ar flow ratio in the ZnO sputtering process the ZnO crystal quality is improved by annealing at a high temperature such as 800 and 1000 °C. It can be easily understood that ZnO grains grow and the densities of the crystallographic defects including dislocations, interstitials and vacancies in the ZnO thin films decrease during high temperature annealing. Therefore, the ZnO crystal quality is improved by high temperature annealing.

In contrast annealing at a low temperature such as 600 °C increases FWHM implying that the crystal quality is aggravated. Grain growth does not occur but recrystallization may occur in the ZnO thin flim during annealing at 600 °C. It should be noted that 600 °C is a relatively low temperature for ZnO annealing because the melting point of ZnO is 1925 °C. The recrystallization temperature for ZnO is in the range of 476–851 °C

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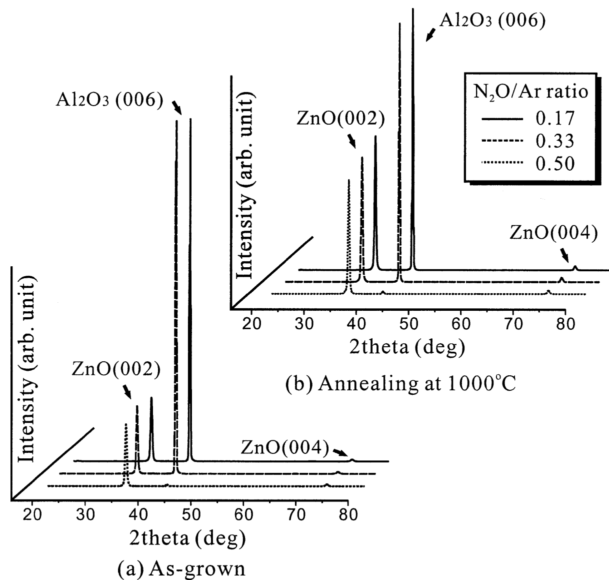

Figure 1 X-ray diffraction spectra for as-grown and annealed ZnO thin films for different N_2O/Ar ratios in the sputtering process.

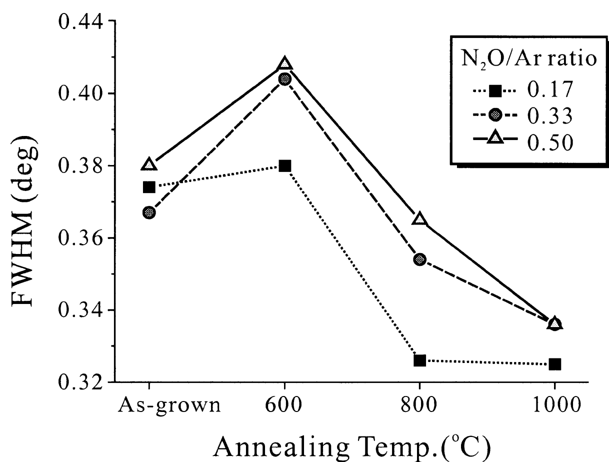

Figure 2 Full width at half maximum (FWHM) of the ZnO (002) diffraction intensity peak for different N_2O/Ar ratios in the sputtering process.

which is equivalent to $T_m/3$–$T_m/2$ where T_m is the melting point of ZnO. Therefore, the grain size of the ZnO thin film can become smaller owing to recrystallization by annealing at 600 °C, which may be a main cause for the decrease in the FWHM of the ZnO (002) peak. We confirmed that the grain size of the ZnO thin film annealed at 600 °C is smaller than that of the as-deposited ZnO thin film by SEM cross-sectional view observations. Besides recrystallization the dislocation density and the concentrations of Zn interstitial and oxygen vacancy will decrease by annealing at 600 °C. This may improve the ZnO crystal quality, but this positive effect seems to be smaller than the negative effect of grain refinement by recrystallization judging from the XRD analytical results that the FWHM of the ZnO (002) diffraction peak deceases by annealing at 600 °C (Fig. 2).

The electron concentrations, mobilities and resistivities of ZnO thin films deposited by magnetron sputtering and then annealed in oxygen atmosphere at 800 and 1000 °C for 1 h are shown in Table I and Fig. 3a, b and c. We can see a trend in these figures that the electron concentration decreases with the increase of

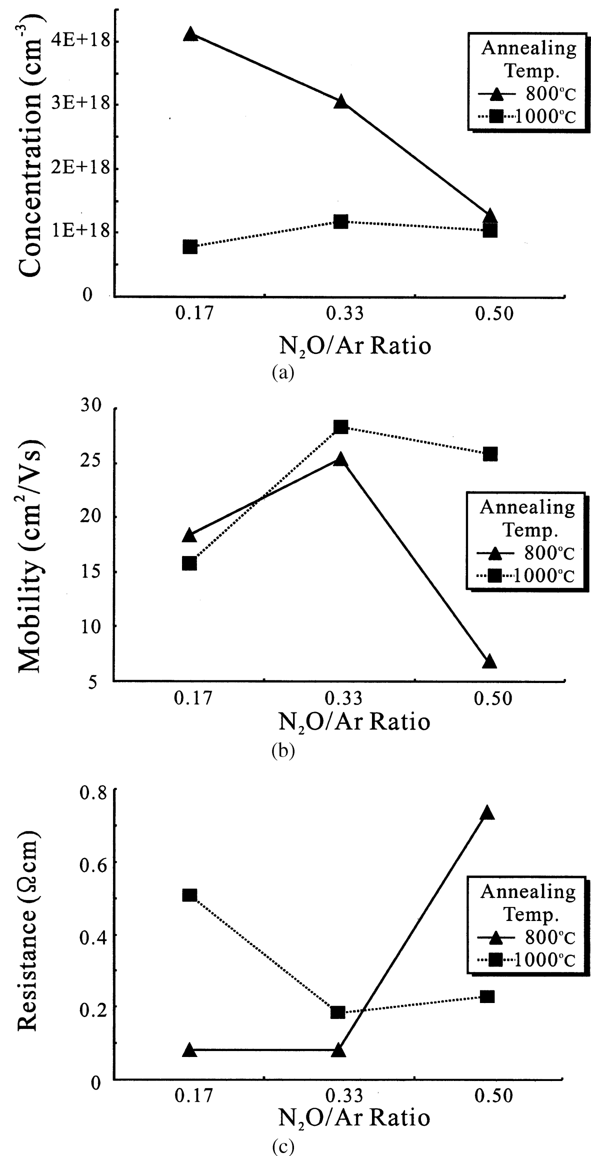

Figure 3 (a) Carrier concentrations, (b) carrier mobilities and (c) resistivities of ZnO thin films deposited by magnetron sputtering and then annealed at 800 or 1000 °C as functions of the N_2O/Ar ratio in the sputtering process.

the N_2O/Ar ratio in the case of 1000 °C annealing, suggesting that increasing the N_2O/Ar ratio could change *n*-type ZnO to *p*-type. These figures tell us two other important things.

First, the electron concentration in the ZnO film nearly does not change as the N_2O/Ar flow ratio in the sputtering process in the case of postannealing at 800 °C, while it decreases significantly in the case of postannealing at 1000 °C (Fig. 3a). This result implies two things. The first that the N_2O/Ar flow ratio should be higher than 0.5 to obtain *p*-type ZnO when the ZnO thin film is annealed at 800 °C. Otherwise, background electrons are not sufficiently compensated, so that the ZnO film will remain unchanged to *p*-type. The other is that even if the N_2O/Ar flow ratio is as low as 0.17, there is a possibility that *p*-type ZnO is obtained if the annealing temperature is high enough.

Second, a very low electron mobility is obtained for the N_2O/Ar flow ratio as high as 0.5 in the ZnO sputtering process when postannealing is conducted

TABLE I Electron concentrations, electron mobilities and resitivities of ZnO films for different N_2O flow rates and annealing temperatures

Sample no.	N_2O flow rate (sccm)	Annealing temp (°C)	Electron conc. (cm^{-3})	Mobility (cm^2/Vs)	Resistivity (Ω cm)
A1	5	800	4.31E+18	18.4	7.86E−02
A2		800	3.94E+18	18.3	8.62E−02
A3		800	3.94E+18	18.3	8.61E−02
B1	10	800	2.99E+18	26.2	7.95E−02
B2		800	3.09E+18	25.0	8.07E−02
B3		800	3.10E+18	24.9	8.04E−02
C1	15	800	1.32E+18	6.5	7.26E−01
C2		800	1.23E+18	6.8	7.40E−01
C3		800	1.31E+18	6.3	7.49E−01
D1	5	1000	7.62E+17	14.5	5.69E−01
D2		1000	7.75E+17	16.3	4.93E−01
D3		1000	8.18E+17	16.3	4.67E−01
E1	10	1000	1.20E+18	13.6	2.42E−01
E2		1000	1.18E+18	28.5	1.84E−01
E3		1000	1.18E+18	28.1	1.88E−01
F1	15	1000	9.67E+17	24.8	2.60E−01
F2		1000	1.12E+18	26.7	2.08E−01
F3		1000	1.09E+18	25.9	2.20E−01

at a temperature as low as 800 °C. However, quite a high electron mobility is obtained, even when the N_2O/Ar flow ratio is as high as 0.5, if the postannealing is conducted at a temperature as high as 1000 °C (Fig. 3b).

The resistivity of and n-type semiconductor is determined by carrier concentration and carrier mobility as in the following equation :

$$\rho = 1/q\mu_n n$$

where ρ, q, μ_n and n represent resistivity, electronic charge, electron mobility and electron concentration, respectively. As shown in Fig. 3c a very high resistivity of the ZnO film deposited by magnetron sputtering with the N_2O/Ar flow ratio of 0.5 is obtained when it is annealed at 800 °C. It is mainly attributed to the low electron mobility (Fig. 3b). However, if it is annealed at a sufficiently high temperature such as 1000 °C or higher, then a ZnO film with quite a low resistivity will be obtained even though the N_2O/Ar ratio in the sputtering process is as high as 5.0.

In summary, high temperature annealing markedly improves the quality of the ZnO crystal grown on the single crystal sapphire substrate by magnetron sputtering. The electron concentration and the mobility in the ZnO film doped more heavily with nitrogen using N_2O plasma decrease more rapidly with the increase of the annealing temperature. This implies that growth of a ZnO thin film with a high nitrogen doping concentration followed by high temperature annealing could change eventually n-type ZnO to p-type ZnO by compensation of the intrinsic n-type defects such as oxygen vacancies and zinc interstitials.

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