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A role of oxygen vacancy on annealed ZnO film in the hydrogen atmosphere

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ABSTRACT

RF-sputtered ZnO films were annealed in the ambient atmospheres of Ar or hydrogen gas. Hydrogen effects on oxygen vacancies of ZnO films were studied through the characterizations of physical and electrical properties after annealing at 300 °C. The carrier concentration was increased to $\sim 10^{17}$ cm^{-3} in both annealing ambient atmospheres. On the other hand, the mobility was distinctly decreased when the films were annealed in the ambient atmosphere of Ar gas. Even though the physical structure undergoes small changes regardless of annealing ambient atmospheres, the increase of oxygen vacancies was remarkably suppressed in the annealing ambient atmosphere of hydrogen gas. Two distinct band edge states, generated by oxygen vacancies, are correlated to the changes in carrier concentration and mobility as a function of energy level below the conduction band.

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1. Introduction

N-type ZnO oxide semiconductor films with wide-band gap (~3.3 eV) have been investigated for a wide range of applications, such as UV light emitters, spintronic devices, transparent high-power electronics, surface acoustic wave devices, piezoelectronic transducers, gas and biological sensors, and solar cells [1–3]. Especially, ZnO-based thin film transistors (TFTs) are very attractive in flexible and transparent electronics because the devices show the moderate hall mobility (>1 cm^2 V^{-1} s^{-1}) even at room temperature and the ZnO semiconductor is transparent in the visible range [4].

Recently, several researchers have reported TFTs application using stoichiometry ZnO semiconductor by various preparation methods [5,6]. However, the devices usually showed high off-current (>10^{-11} A) and poor on/off ratio of drain current, since the resistivity of ZnO film is very sensitive on the chemical bonding states including oxygen vacancies during the deposition or post-treatment. Therefore, most of interest is focused on the control and modification of ZnO semiconducting properties, such as carrier concentration and mobility, using simple process conditions and annealing at low temperature (~300 °C). The control of various properties in ZnO films was achieved by impurities doping, ion implantation, annealing process and the other methods [7,8]. However, the impurities doping or ion implantation are able to produce the unexpected bonding states and the collision damage into ZnO matrix, which can generate unnecessary and uncontrollable defect states [9]. Our group has already reported the thermal evolution of band edge states for ZnO films and their connection with electrical properties [10]. Even though a role of hydrogen is very important for the changes in conducting properties of oxide semiconductors, the previous researches have included the insufficient results for hydrogen effects on the modulation of electrical properties, and their correlations with physical properties in ZnO system [11].

In this study, we investigate the changes in oxygen vacancies of ZnO films as comparing annealing in hydrogen atmosphere with that in Ar atmosphere, using characterizations of physical and electrical properties. Moreover, physical correlations between oxygen vacancies and electrical properties of ZnO films are spectroscopically studied.

2. Experiment

Si wafers with thermally grown SiO_2 (100 nm) were used as substrates onto which ZnO films (50 nm) were deposited by a radio frequency (RF) sputtering system. The detailed process conditions for deposition using RF sputtering system are summarized in Table 1. Then, ZnO films were annealed in the ambient atmospheres of Ar or hydrogen gas by a furnace system for 1 h and at 300 °C. The

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Table 1
Process conditions of the RF sputtering system for the deposition of ZnO films.

Process parameters	Value
RF power	75 W
Ar gas	50 sccm
Substrate temperature	Room temperature
Distance between target and substrate	145 mm
Rotation speed	4 rpm
Base pressure	2.5×10^{-6} Torr
Working pressure	10 mTorr

annealing ambient atmospheres of Ar or hydrogen gas were controlled by mass flow controller with the flow rate of 100 sccm.

Hall measurements were employed to investigate the electrical properties of films, such as carrier concentration and mobility. The physical structure of the annealed ZnO films was observed by conventional theta–2theta X-ray diffraction (XRD) measurement. The chemical bonding states were investigated by X-ray photoemission spectroscopy (XPS). The detailed electronic structures, related to changes in band gap and band edge state below the conduction band, were analyzed by spectroscopic ellipsometry (SE). The SE measurement was performed by a rotating analyzer system with an auto retarder in the energy range of 0.75 eV–6.4 eV with incident angles of 65°, 70°, and 75°.

3. Results and discussion

Fig. 1 shows the electrical properties obtained by Hall measurement, including (a) the carrier concentration and (b) mobility of the ZnO films annealed in the ambient atmospheres of Ar and hydrogen gas at 300 °C. In as-deposited ZnO film, the carrier concentration and mobility were 1.2×10^{14} cm^{-3} and 107 $cm^2\ V^{-1}\ s^{-1}$, respectively, and the films displayed *N*-type semiconductor characteristic. When the annealing temperature was increased to 300 °C in the ambient atmospheres of Ar or hydrogen gas, the carrier concentration was increased to $\sim 10^{17}$ cm^{-3}. The mobility of ZnO film annealed in the hydrogen atmosphere, was changed into $\sim$30 $cm^2\ V^{-1}\ s^{-1}$, while that annealed in the Ar atmosphere was drastically decreased to 0.21 $cm^2\ V^{-1}\ s^{-1}$. These remarkable changes in carrier concentration and mobility could be associated with the evolution of carrier and the hindrance of charge transport by the generation of defect states such as oxygen vacancies, which are affected by the annealing process [12].

Fig. 2 shows the XRD data of the ZnO films annealed in an ambient atmospheres of Ar or hydrogen gas. In the as-deposited and annealed ZnO films, the preferred orientation of a hexagonal

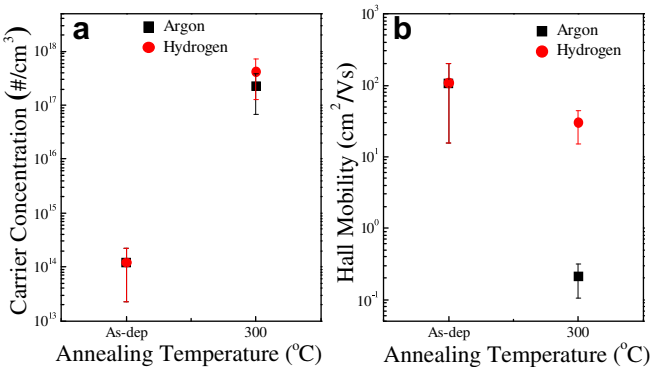

Fig. 1. (a) Carrier concentration and (b) hall mobility of the as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C.

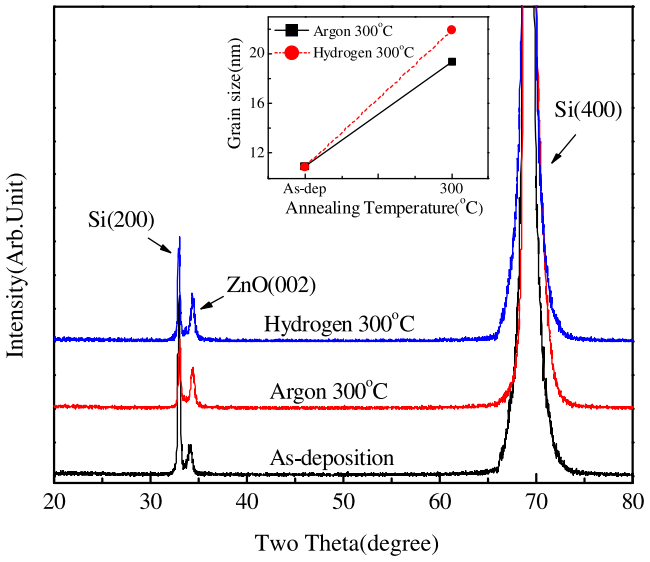

Fig. 2. XRD data collected from the as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C. Inset is the calculated results for grain size.

ZnO (002) phase was observed, regardless of annealing ambient atmospheres. The crystalline ZnO (002) peak is maintained without any structural transformation or with the minute increase of preferred orientation up to an annealing temperature of 300 °C. On the other hand, the calculated grain size is increased as shown in the inset of Fig. 2, in both annealing ambient atmospheres. The bigger grain size induces the enhancement of mobility due to the reduction of grain boundary [13]. Comparing the changes in grain size with mobility shown in Fig. 1, there is the discrepancy that the mobility is degraded with the increase of grain size. These mean that another origin like defect states such as oxygen vacancies might dominantly cause the decrease of mobility in addition to the effects of bigger grain size.

The changes in chemical bonding state related to oxygen were investigated through XPS measurement of O 1s spectra for as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas. XPS spectra were obtained after sputtering by Ne in order to minimize the surface contamination of adsorbed OH, C, H_2O and so on. In order to examine the detailed oxygen states, O 1s spectra shown in Fig. 3(a) were carefully deconvoluted into 3 peaks (O1, O2, O3), using Gaussian fitting with the subtraction of Shirley type background and considering the previous report [14]. O1 peak in the low binding energy of the O 1*s* spectrum is attributed to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array, which indicates the Zn–O bonds. The higher binding energy (O3) around 532.8 eV is usually attributed to chemisorbed or dissociated oxygen or OH species on the surface of the ZnO films, such as $-CO_3$, adsorbed H_2O or adsorbed O_2. The component at the medium binding energy (O2) of the O 1s spectrum is associated with O^{2-} ions that are in oxygen-deficient Zn–O bonding matrix. As a result, changes in the intensity of O2 peak may be in connection with the variations in the concentration of the oxygen vacancies (V_O) [14]. Fig. 3(b) presents the relative intensity of O2 peak for the as-deposited and annealed ZnO films in the ambient atmospheres of Ar and hydrogen gas. The relative intensity of O2 peak is remarkably increased in the annealed film in Ar atmosphere, but that of the annealed film in hydrogen atmosphere has much smaller increase, which means that the amount of oxygen vacancies increase upon annealing in the Ar atmosphere.

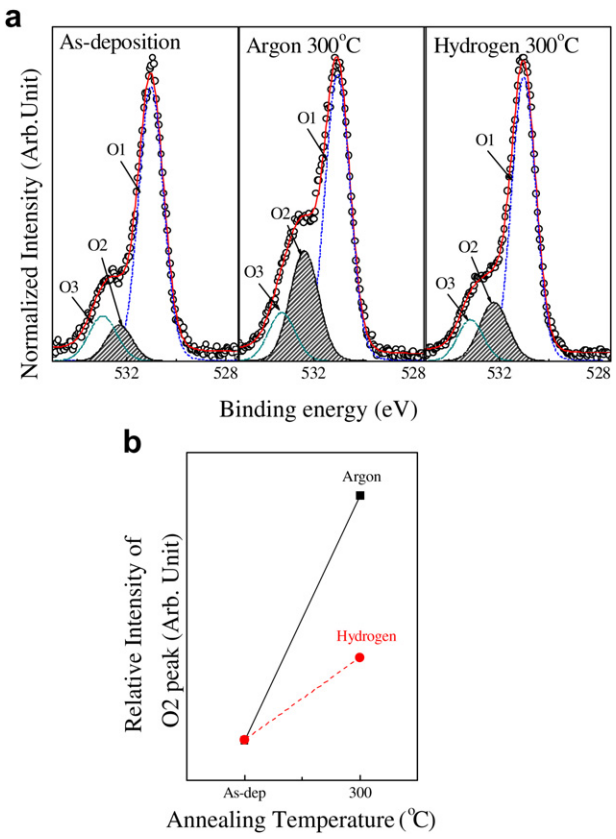

Fig. 3. (a) XPS spectra of O 1s for as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C. Spectra were deconvoluted into the detailed O1, O2, and O3 states. (b) Relative intensity of O2 state (oxygen vacancies) for as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C.

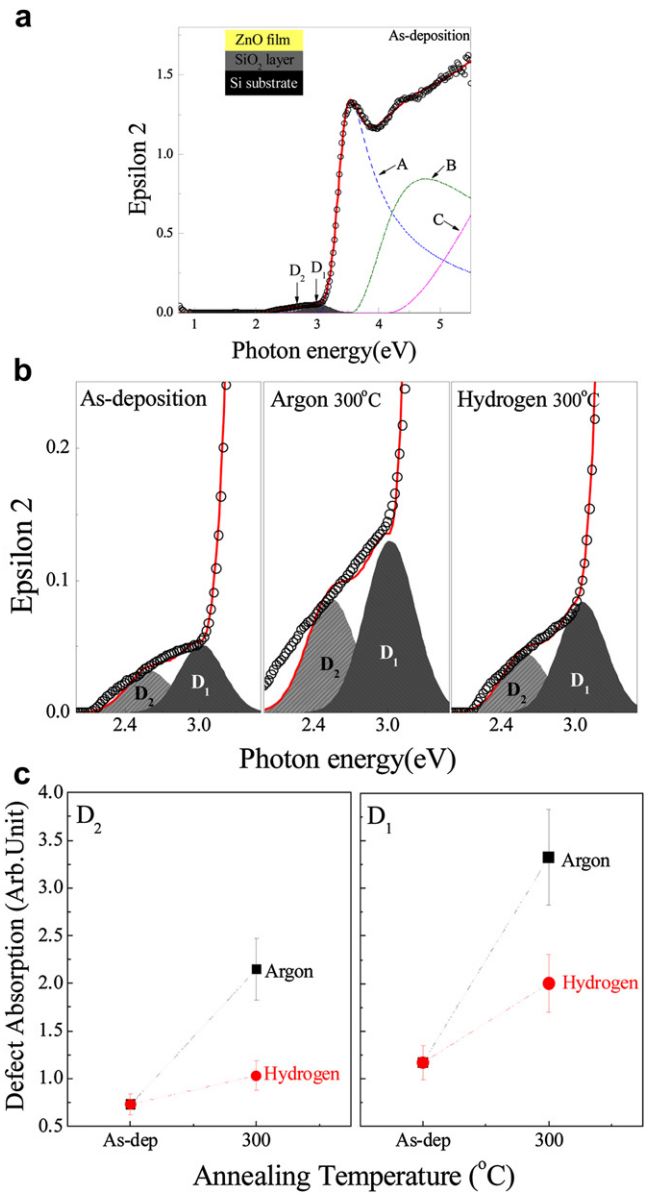

Fig. 4. (a) Imaginary dielectric function (ε_2) spectra from SE measurements for the as-deposited ZnO film. These spectra were extracted from a simple four-phase model as shown in the inset. The deconvoluted peaks, labeled A, B, and C are model fits using Tauc–Lorentz function and two distinct deconvoluted peaks, labeled D_1 and D_2 are Gaussian fits and represent the band edge states located below the conduction band edge. (b) Enlargement of the band edge states (oxygen vacancies) below the conduction band edge for as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C. (c) Relative absorption for two distinct band edge states (D_1 and D_2), calculated by the Gaussian fits in (b).

In order to investigate the electronic structure of the ZnO films, including the oxygen vacancies as a function of energy level below the conduction band edge, SE measurements were carried out for as-deposited and annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas. The imaginary dielectric function (ε_2) spectra for the as-deposited ZnO film on Si substrates are shown in Fig. 4(a). These spectra were extracted from a simple four-phase model, which is comprised of a Si substrate, SiO_2 overlayer, ZnO overlayer, and an ambient layer as shown in the inset of Fig. 4(a) [15]. The features that can be seen at the onset energy above the optical band gap around ~3.1 eV indicate the conduction band states of the ZnO, which correspond to the hybridized molecular orbital states mixed by the Zn 4sp and O 2p states [16,17]. A detailed and quantitative analysis of the band edge states and conduction band states was performed by fitting using a Gaussian model (band edge states) and a Tauc–Lorentz model (conduction band states). The detailed fitting parameters are summarized in the previous report by Park et al. [10] The Gaussian model fits are comprised of two distinct band edge states related to oxygen vacancies with a shallow band edge state (D_1) and deep band edge state (D_2), which are located at 0.08 eV and 0.60 eV away from the conduction band edge, respectively. Fig. 4(b) and (c) represent the narrow region of the band edge states below the conduction band edge and the relative defect absorption of band edge states (D_1 and D_2) of the ZnO films annealed in the ambient atmosphere of Ar or hydrogen gas at 300 °C.

Based on the analysis in Fig. 4, the quantitative amount of oxygen vacancies is higher for the annealed ZnO film in Ar atmosphere rather than the as-deposited and annealed films in hydrogen atmosphere, which is similar to the results for O2 peak of XPS spectra in Fig. 3. When considering the previous electrical data, the variation of oxygen vacancies in D_1 and D_2 states is strongly correlated with the increase of carrier concentration and the degradation of mobility. The plausible origin of the changes in electrical properties such as carrier concentration and mobility could be attributed to the evolution of the band edge states related to oxygen vacancies in the different annealing ambient atmospheres [18]. The increase of carrier concentration with annealing in an ambient atmosphere of Ar gas, may be explained by the increase of oxygen vacancy in the shallow band edge state (D_1)

because it is regarded that the number of free electron which can conduct as a carrier is getting lager by the generation of oxygen vacancy [19]. However, it is difficult to interpret that the increase of carrier concentration with annealing in hydrogen atmosphere is only related to the changes of D_1 states. Even if the shallow band edge state (D_1) is slightly increased in the film annealed in hydrogen atmosphere, this case could be understood by adding a role of hydrogen, which can exist in interstitial and substitutional sites of Zn–O bonding matrix and can function as a donor. The carrier generated by excess electron of hydrogen donor could be induced by annealing in hydrogen atmosphere through the following process : $H -> H^+ + e^-$ [20].

The oxygen vacancy in the deep band edge state (D_2) can cause the charge trapping and the increase in charge scattering during carrier transport due to energy levels far from the conduction band [21]. Thus, the increase of oxygen vacancies in the deep band edge results in the decrease of mobility for the annealed ZnO film in the ambient atmosphere of Ar gas. From the above interpretations, the changes in the band edge states, induced by oxygen vacancies, contribute to the modification of the carrier concentration and mobility in annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas.

4. Conclusions

The annealed ZnO films in the ambient atmospheres of Ar or hydrogen gas at 300 °C, were studied using the various physical and electrical characterization. The annealing of ZnO films in the ambient atmospheres of Ar or hydrogen gas results in the increase of carrier concentration with $\sim 10^{17}$ cm^{-3}. However, the mobility undergoes small decrease in ZnO film annealed in the ambient atmosphere of hydrogen gas, while is drastically degraded to 0.21 cm^2/V when the film is annealed in the ambient atmosphere of Ar gas. The physical structure is preserved, with the crystalline oriented by the hexagonal ZnO (002) phase, regardless of annealing ambient atmospheres. On the other hand, the chemical bonding states of oxygen are distinctly changed with the increase of oxygen vacancies in the annealing ambient atmosphere of Ar gas. The oxygen vacancies could be spectroscopically distinguished into two different band edge states in shallow and deep energy level below the conduction band and they are correlated to the changes in carrier concentration and mobility. The increase of carrier concentration for ZnO film annealed in the ambient atmosphere of Ar gas is related to the increase of oxygen vacancy in the shallow band edge state, and that of the film annealed in the ambient atmosphere of hydrogen gas could be affected by excess electron of hydrogen dissociation in addition to the slight increase of oxygen vacancy in the shallow energy region. The remarkable degradation of mobility in the annealing of Ar ambient atmosphere is associated with the increase of oxygen vacancy in the deep band edge state.

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