Short Note

Optical property and crystallinities of Si doped β-Ga_2O_3 thin films

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Abstract A transparent electrode of β-Ga_2O_3 films for solar cells, flat panel displays and other devices, which consist in chemically abundant and ecological elements of gallium and oxygen, were grow on quarts or silicon substrate by RF magnetron sputtering using sintered Ga_2O_3 target. The polycrystalline β-Ga_2O_3 grew by the thermal annealing after RF sputtering. It is important that oxygen introduction at the sputtering to obtain flat β-Ga_2O_3 film. The optical absorption coefficient over energy gap increased with decreasing Ar/O_2 ratio. The impurity of Si was also doped into the grown films. From the measurement of optical absorption coefficient, it is concluded that the β-Ga_2O_3 energy gap increases with increasing Si concentration in the deposited film.

Keywords : Gallium oxide, transparent electrode, optical absorption spectra

1. Introduction

Most of the compound semiconductors contain toxic and/or rare elements and are therefore becoming harmful for the user and/or the earth environment. For these reasons, the development of devices composed of chemically abundant and ecological materials is an urgent research target. The scarce element of indium is contained in tin doped indium oxides (ITO). ITO is mainly used as ingredient for the transparent electrode materials of solar cells and various opto-electrical devices. It has demerits that like the toxic and life of resources is short. Therefore, ZnO and SnO_2 or the other materials are considered for the alternative materials of ITO [1].

Gallium oxide (β-Ga_2O_3) is a wide band gap semiconductor about 5.0 eV [2 - 4]. Application of β-Ga_2O_3 has been expected that the transparent electrode or a gas sensor, because of electric conductivity of the β-Ga_2O_3 increases by tin doping [4, 5]. We have grown β-Ga_2O_3 films by sputtering, and evaluated crystalline and electrical properties [6]. However, resistivity of the film was still high (> few MΩcm). The aim of this research is to reduce the resistivity of a β-Ga_2O_3 film. In this article we have try some studies, to reduce the β-Ga_2O_3 reisistivity. These are optimize growth condition of the film and impurity doping. Oxygen gas at the sputtering is important for oxide material. Then, influence of crystalline qualities of β-Ga_2O_3 film of oxygen introduce rate at sputtering is studied. Also, Si doped β-Ga_2O_3 film is grown to reduce resistibity of the film. It is expected that the Si behave as a donor in the β-Ga_2O_3, because of it is group IV elements as same as tin. Undoped β-Ga_2O_3 film become n-type, its origin is known oxygen vacancy. [7] Therefore, to increase carrier density in the β-Ga_2O_3, high-energy electrons were irradiated to the film. It is expected that the defects in the β-Ga_2O_3 are formed by the electron irradiation, and it behave the origin of carriers.

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2. Experimental

The β-Ga_2O_3 films were grown on a Si (001) or quartz substrate by RF magnetron sputtering [6]. For the sample for XRD measurements, the substrate used Si. And the quarts substrate used for optical absorption and the other measurements. The used target was 5N-sintered Ga_2O_3. After substrate cleaning, sputtering was performed in an argon or argon/oxygen ambient for 10 min at 2 Pa. To investigate influence of oxygen composition in the sputtering ambient, argon/oxygen (Ar/O_2) ratio varied from 0 to 1.0 in partial pressure. The thickness of the film was about 30 nm for 10 min deposition. The substrate temperature was fixed at room temperature during the deposition. To add the impurities into the β-Ga_2O_3 films, mm-size Si pieces were put on the target during the sputtering. Therefore, the target and the impurity were co-sputtered, and co-deposited on the substrate. Unfortunately, actual doping concentration of Si in β-Ga_2O_3 could not measure, yet. After the deposition, the samples were annealed at 600˚C for 15 min in nitrogen to improve the crystalline quality of the films.

To investigate the crystalline quality of the samples, cross-sections and surface morphology were observed using scanning electron microscope (SEM) and θ-2θ x-ray diffraction (XRD). The diffraction angle was varied from 2θ=20˚ to 80˚. To investigate the optical absorption spectra, the films were measured at RT using a SHIMADZU UV-2200 spectrometer. To eliminate the influence of the quartz substrate, reference spectra of the quartz substrate were measured and subtracted from the optical absorption spectra of the sample. The incident light wavelength was varied from 190 to 900 nm.

3. Results and discussions

As deposited sample surface is smooth, because crystallinity of the Ga_2O_3 film is amorphous (not shown). However, the sample

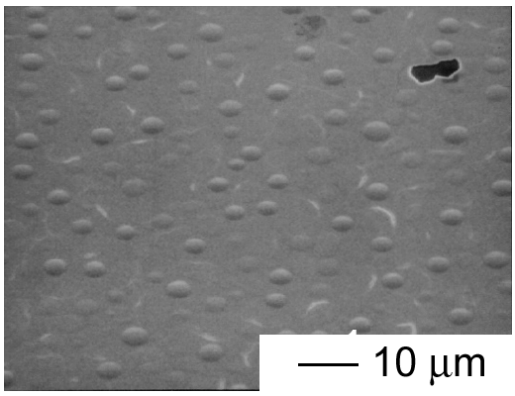

Figure 1. SEM photograph of the undoped β-Ga_2O_3 surfaces sputtered in Ar ambient.

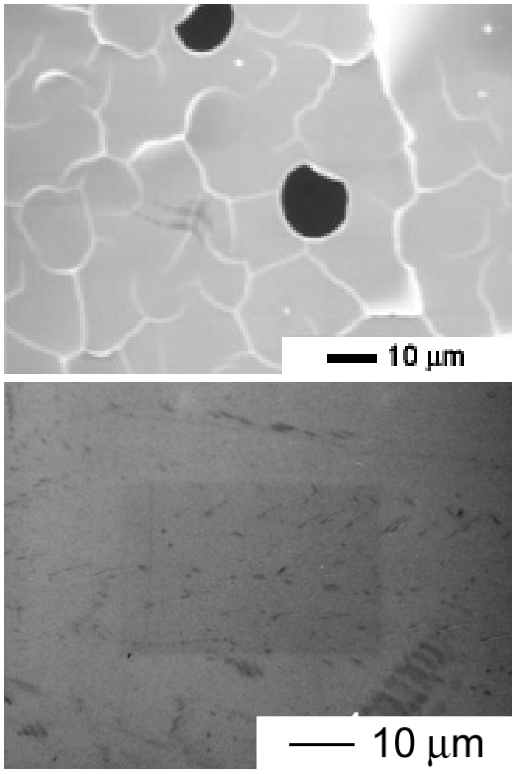

Figure 2: Plane view of β-Ga_2O_3 surface of a sample sputtered in an argon/oxygen ambient and annealed at 600˚C for 10 min.

sputtered in Ar/O_2 = 1.0 (i.e. Ar ambient), after the 600˚C annealing there are many protrusions on the sample surface as shown in SEM photograph (Fig. 1). It was surmised that oxygen deficiency during sputtering produces the protrusions. Therefore, the sputter ambient was changed to an argon/oxygen gas mixture. Figure 2 show the surface SEM photographs of the sample sputtered in an argon/oxygen ambient and annealed at 600˚C for 10 min. The ratio of argon and oxygen is (a) Ar/O_2 = 0.8 and (b) Ar/O_2 = 0.6, respectively. The surface flatness improved by changing the sputtering ambient. For the sample with Ar/O_2 = 0.8 (Fig. 2(a)), cracks are observed. Although, for the sample with Ar/O_2 = 0.6 (Fig. 2(b)), quite flat surface is obtained.

The crystalline qualities of the β-Ga_2O_3 films with different sputtering condition (argon/oxygen pressure) were evaluated by XRD θ-2θ measurement as shown in Fig. 3. After the annealing, peak at 2θ=61.7˚ peak corresponds a β-Ga_2O_3 (120) appeared in the XRD patterns as shown in Fig 3. The peak intensities do not change the Ar/O_2 ratios. From this result, deference of crystalline quality by sputtering ambient could not observed. The peak at 2θ=65.9˚, which is marked as "*" in the figure, appeared for all samples. It does not match the diffractions from β-Ga_2O_3, therefore, one possibility considered is that the peak corresponds to the other material.

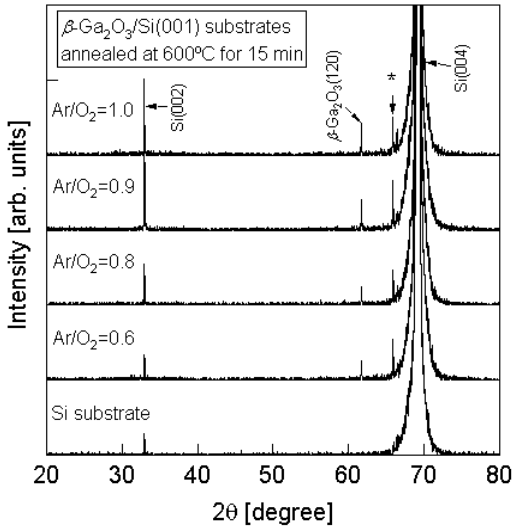

Figure 3: XRD patterns of undoped β-Ga_2O_3 thin films sputtered in an argon or argon/oxygen ambient and after the 600˚C annealing.

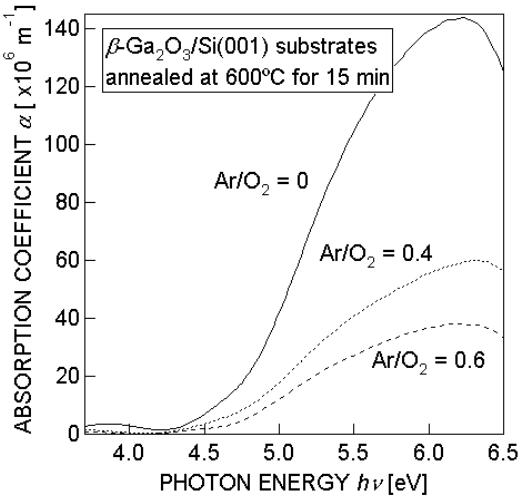

Figure 4: Optical absorption coefficients against incident photon energy for Ar/O_2 = 0, 0.4 and 0.6, respectively.

Figure 4 shows optical absorption coefficients against incident photon energy for Ar/O_2 = 0, 0.4 and 0.6 samples, respectively. For the samples that sputtered high Ar partial pressure Ar/O_2 = 0.8, 0.9 and 1.0, absorption spectra could not obtained enough transmitted photon intensity for detection, because the surface conditions of the surface are bad. Also, for the as-deposited films, the clear optical absorption spectra do not obtain, because these films are amorphous. The absorption coefficient decreases with decreasing oxygen partial pressure (increasing Ar/O_2 ratio) at the sputtering. This change corresponds to difference of oxygen.

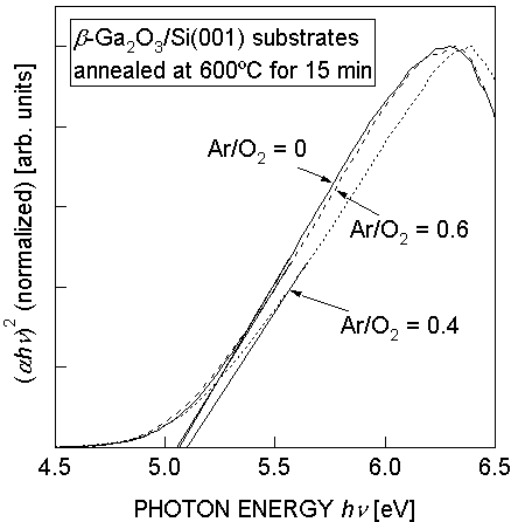

Figure 5: $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films annealed at 600˚C for 15 min.

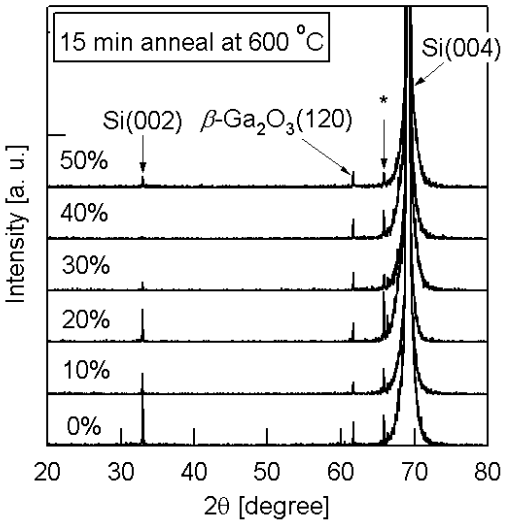

Figure 6. XRD θ-2θ patterns for Si substrate and 0 to 50%-Si doped β-Ga_2O_3 films.

deficient in the β-Ga_2O_3 film for each sample. The energy gaps of these films were measured from optical absorption spectrum.

Figure 5 shows $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films. The estimated energy gaps are 5.04 eV (Ar/O_2 = 0), 5.08 eV (Ar/O_2 = 0.4) and 5.05 eV (Ar/O_2 = 0.6), respectively, and correspond to reported values of β-Ga_2O_3 bulks or films. There are no differences about energy gaps with sputtering ambient.

Next, influences of Si doping into the β-Ga_2O_3 film are discussed. The crystalline quality of the Si doped β-Ga_2O_3 films was evaluated by XRD θ-2θ measurement as shown in Fig. 6. The Si doping level varied from 0 to 50 % and the XRD pattern of the Si substrate is shown in the same figure. After the annealing, a β-Ga_2O_3 (120) peak at 2θ=61.7˚ appeared in the XRD patterns as shown in Fig. 3. There is some possibility that β-Ga_2O_3 and Si complexes are formed in the film by Si doping. However, it could not be decided quantitatively with which mixture the peak corresponds.

Optical absorption spectra for the different β-Ga_2O_3 films are shown in Fig. 7. For the as deposited films (non annealed), the clear optical absorption spectra do not obtain, because these films are amorphous. The maximum value of the absorption coefficient decreases with increasing Si doping. This change is caused by the formation of other phases and/or defects. Also, it seems that the peak position of the absorption coefficient shifts to higher energies by Si doping.

Figure 8 shows $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films. The energy gap of an undoped β-Ga_2O_3 film is found to be about 5.0 eV. This value is in agreement with the reported values for undoped β-Ga_2O_3. The energy gaps which calculated from $(\alpha h\nu)^2$ versus photon energy plots with Si composition are shown in Fig. 6. clearly increases with increasing Si concentration. For the 50 %-Si doped β-Ga_2O_3 film, the energy gap is 6.1 eV. The increase in the band gap value (1.1 eV) is quite large. Then, the result suggests that another phase than β-Ga_2O_3 is expected to be formed in the films, however, this was not observed in the XRD patterns.

Finally, influence of Si doping for resistivities of the β-Ga_2O_3

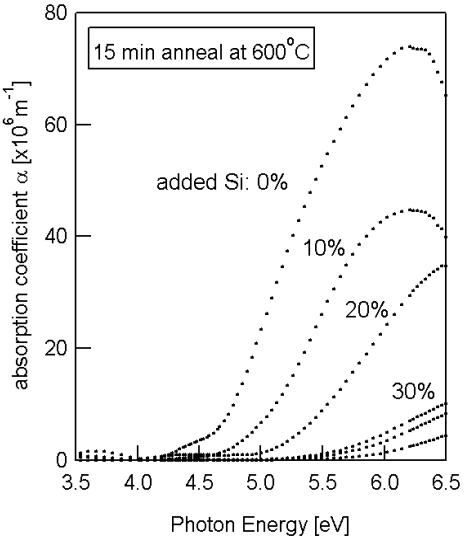

Figure 7. Optical absorption spectra for β-Ga_2O_3 films after the annealing at 600˚C for 15 min.

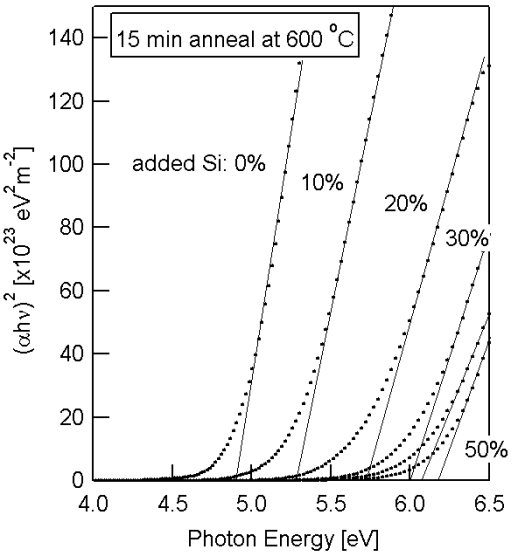

Figure. 8. $(\alpha h\nu)^2$ versus photon energy versus plots of the β-Ga_2O_3 films annealed at 600˚C for 15 min.

films are investigated. For the undoped β-Ga_2O_3 film, resistivity is 1.18 MΩcm, and it is very high. Therefore, impurity doping into the β-Ga_2O_3 film attempted by co-sputtering of Si and Ga_2O_3 targets. Figure 6 shows the resistivities of Si doped β-Ga_2O_3 films against doped Si composition. At low compositions (10 and 30 %) the resistivitiy increase as shown in Fig. 9, while the resistivity decreases at 50 % doping. The resistivities of doped β-Ga_2O_3 do not decrease with undoped value, and the result fell short of the expectation. There are some possibilities that β-Ga_2O_3 and Si complexes are formed in the film by Si doping, and the resistivity increases. After the annealing, for the all Si doped samples, the β-Ga_2O_3 films grown on substrates and no other phases are observed by XRD measurement. It needed additional considerations as doping composition, material and the other conditions, to decrease resistivity of the β-Ga_2O_3 films by impurity doping.

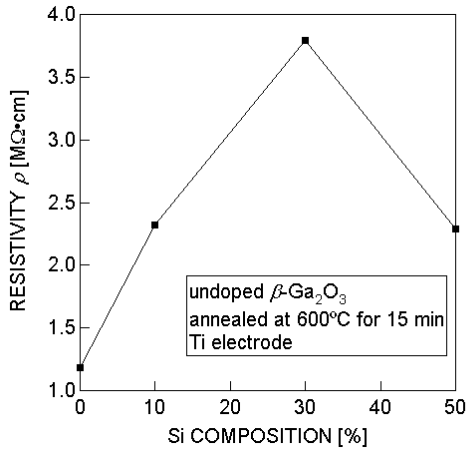

Figure 9: Resistivities of Si doped β-Ga_2O_3 films against doped Si composition.

4. Conclusion

Impurity added β-Ga_2O_3 thin films were grown on Si (001) substrates by sputtering. The band gap of the undoped β-Ga_2O_3 is about 5.0 eV, evaluated from the optical absorption spectra, while the band gap of impurity added samples is shifted towards higher energy (about 1.1 eV). Also, for impurity added samples, optical absorptions corresponding to the impurity addition are observed in the band gap.

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