Fabrication and opto-electrical properties of amorphous (Zn,B)O thin film by pulsed laser deposition

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Growth of amorphous ZnO by B doping and their opto-electrical properties are reported. The B-doped ZnO (ZnO:B) films were grown by pulsed laser deposition using polycrystalline ZnO:B ceramic targets. Although the solubility limit of B in bulk ZnO polycrystal was ~4%, 18%-doped ZnO:B showed the shrinkage in the c-axis length. Preferentially (002)-oriented polycrystalline ZnO:B films were grown for the B concentration [B] ≤ 18%; while, amorphous ZnO:B films were obtained for [B] ≥ 26%. It was found that the density of the amorphous ZnO:B film was smaller by 9% than that of crystalline ZnO (5.61 g·cm⁻³), which is explained mainly by the incorporation of the light B atoms. The optical bandgap of the amorphous ZnO:B thin film was ~3.38 eV. The amorphous ZnO:B films have low free electron density of ~10¹⁵ cm⁻³, suggesting the existence of electron traps. Hall mobility of the amorphous ZnO:B (~1 cm²(V·s)⁻¹) was smaller than those of the polycrystalline ZnO:B films.

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1. Introduction

Transparent conducting oxide (TCO) films have attracted much attention due to their good transparency for human eyes and high conductivity, and thus they are widely used as transparent electrodes in a wide range of electronic devices.¹⁻⁴ For the transparent electrode purpose, impurity dopants such as B, Al, In, Ga, and Sn are employed for ZnO to increase the electron density and conductivity by keeping high transparency.⁵⁻⁷ On the other hand, amorphous oxide semiconductors (AOSs), represented as amorphous In–Ga–Zn–O (a–IGZO), are now employed for channel materials in thin-film transistors (TFTs) of state-of-the-art flat-panel displays due to their superior properties such as high mobilities [≥10 cm²(V·s)⁻¹] and small subthreshold voltage swings (<0.2 V·decade⁻¹) compared with conventional a–Si:H TFTs.⁸⁻¹⁰ Further, a big advantage of AOS TFTs comes from its amorphous structure; polycrystalline Si TFTs suffer from non-uniformity issues due to the grain boundaries.¹¹⁻¹³ While amorphous TFTs such as a–Si:H TFTs and AOS TFTs are free from the grain boundary issues and produce very uniform TFTs,¹⁴⁻¹⁵ Since late 1990’s, research for ZnO-based TFTs revisited and has been investigated intensively; however, polycrystalline ZnO TFTs still suffer from the grain boundary issues and remain to be improved.¹⁶⁻¹⁷ Therefore, amorphous ZnO TFT is considered to be important and promising; however, ZnO forms very stable crystalline phase and, in general, amorphous ZnO is not obtained even if a thin film is grown at room temperature.¹⁹ Only a few papers have been reported for growth of amorphous ZnO, but only very thin (10 nm) films¹⁹ and using cooled substrate during deposition.²⁰ However, it is difficult to apply these methods to practical application. To obtain a stable amorphous phase, it is considered that doping with different valence and different size ions is effective as known in glass science and AOSs. Therefore, doping to ZnO has been examined such as ZnO(N₂).²¹ In this case, the highly covalent bond of N than O would be effective to form the amorphous ZnO. With this line, we expected that B doping to Zn site would also be effective. B-doped ZnO (ZnO:B) has been examined as transparent electrodes for solar cells;²²⁻²³ however, all the films are polycrystalline because high-temperature growth was employed to attain better crystallinity and higher conductivity, and the polycrystalline structure is preferred for thin-film solar cells because the rough surface is good for optical scattering and optical confinement effect to improve energy conversion efficiency.

In this work, we grow ZnO:B films at room temperature by pulsed laser deposition (PLD) in order to grow amorphous phase films. The film structure, film density, electrical properties, and optical band gaps were examined systematically with the B concentration ([B]).

2. Experimental

ZnO:B thin films were deposited on silica-glass substrates by PLD method with (Zn₁₋ₓBₓ)O (x = 0–0.25) polycrystalline ceramic targets. The ZnO:B ceramic targets were prepared from mixed powders of ZnO (purity, 99.9999%) and B₂O₃ (purity,
99.99% sintered at 1000°C for 5 h in atmosphere. Before the film fabrication, the base pressure ($P_0$) of the deposition chamber was evacuated to be $P_0 < 1.0 \times 10^{-5}$ Pa. Approximately 100 nm thick ZnO:B films were deposited under varied oxygen pressures $P_{O_2} = 1$, 3, and 5 Pa at room temperature. A KrF excimer laser (wavelength: 248 nm, repetition rate of 10 Hz, pulsed energy density of 2.3 J cm$^{-2}$) was used as an exciting source.

The structures of the ZnO:B targets and the ZnO:B films were investigated by conventional powder X-ray diffraction (XRD, using Rigaku RINT-2500) with Cu K$\alpha$ radiation. The grazing-incidence X-ray reflectivity (GIXRR, Rigaku SmartLab) was used for measuring film thickness and density. The chemical composition of the targets and the films were measured by X-ray fluorescence spectroscopy. Optical absorption coefficient ($\alpha$) were evaluated by $\exp(-\alpha d) = T/(1 - R)$ with reflection correction, where $T$ is the transmittance, $R$ the reflectance, and $d$ the film thickness [$T$ and $R$ were measured with a UV–Visible-IR spectrophotometer (UV–Vis-IR, Hitachi U-4100)]. Electrical properties such as conductivity ($\sigma$), carrier concentration ($N_e$), and Hall mobility ($\mu_{Hall}$) were examined by Hall effect measurement (TOYO, ResiTec 8300) using the van der Pauw configuration at RT.

3. Results and discussion

3.1 Structural analysis

Figure 1 shows the XRD patterns of the ZnO:B PLD targets with varied B$_2$O$_3$ doping concentration. All the targets are polycrystalline, and only diffraction peaks from pure wurtzite ZnO phase (indicated by circles) are detected for the B$_2$O$_3$ concentrations up to 2%. On the other hand, extra peaks (indicated by triangles), which are attributed to be $\beta$-Zn$_3$(BO$_3$)$_2$ phase, were observed for the B$_2$O$_3$ concentration 5 mol% and higher. As increasing the doping concentration, the intensities of the extra peaks increased, while those from the ZnO phase decreased. This result indicates that the solubility limit of B in ZnO is ~4% for bulk polycrystal synthesized at 1000°C.

Figure 2(a) shows the XRD patterns of the ZnO:B films deposited at $P_{O_2} = 3$ Pa as a function of [B]. The halo peak around 22° comes from the silica-glass substrate. Only 00$l$ diffractions from wurzite ZnO are observed for the ZnO:B films with [B] up to 18%, indicating that these ZnO:B films are polycrystalline with highly c-axis preferential orientation. The 002 diffraction angle was almost unchanged at 34.33° for [B] = 0–10%, while shifted to higher angles to 34.57° for [B] = 18%, indicating that B atoms are incorporated in the polycrystalline ZnO:B films and reduces the c-axis lattice parameter.\cite{25} As [B] increased to 26%, no sharp diffraction peak was detected, indicating that the ZnO:B film became amorphous. To further confirm the amorphous structure, magnified XRD patterns around 35° for the amorphous ZnO:B films ([B] = 26%) with different thickness (~100 and ~300 nm) are shown in Fig. 2(b). As the halo intensity appear to be almost proportional to the film thickness, we can safely attribute it to the amorphous ZnO:B phase.

3.2 GIXRR spectra and film density

Figure 3 shows the GIXRR spectra of the ZnO:B films deposited at $P_{O_2} = 3$ Pa and varied [B] from 0–26%. The GIXRR spectra were analyzed using a trilayer model (surface roughness layer/bulk film layer/silica-glass substrate), which provided the information on film thickness, density, and surface roughness. Generally, the film density can be obtained from the critical angle of the total reflection as indicated in the inset figure. The film density of the undoped ZnO film was analyzed to be ~5.64 g cm$^{-3}$, which agrees well with the reported value of ~5.61 g cm$^{-3}$ for pure crystalline ZnO. Because the critical angle did not change as seen in the magnitude view (inset) up to [B] = 18%, the density was almost unchanged irrespective of [B] as long as the film maintained the polycrystalline structure. On the other hand, the density was decreased significantly to ~5.11 g cm$^{-3}$ when [B] was increased to 26% and the film become amorphous. It indicated that the density of the amorphous ZnO:B is ~9% smaller that of the crystalline ZnO. It would be worth comparing with a-IGZO; the density of a-InGaZnO$_4$ films is ~4% smaller that of crystalline InGaZnO$_4$.\cite{10} As the amorphous

Fig. 1. Powder XRD patterns of ZnO:B ceramic targets with different B$_2$O$_3$ concentration from 0 to 15 mol%. The peaks indicated by circles are attributed to wurzite ZnO phase, while those by triangles to $\beta$-Zn$_3$(BO$_3$)$_2$.

Fig. 2. XRD patterns of ZnO:B films. (a) Wide-range XRD patterns as a function of [B], and (b) magnified XRD patterns for ZnO:B films with [B] = 26% with different film thicknesses (100 and 300 nm).

Fig. 3. GIXRR spectra of ZnO:B films deposited at $P_{O_2} = 3$ Pa and [B] = 0–26%. Inset shows magnified views around the critical angles of the total reflection.
3.3 Optical properties and bandgap variation

Figure 4(a) shows the optical absorption ($\alpha$) spectra of the ZnO:B films with [B] = 0–26%. It is clearly seen that the $\alpha$ spectra were almost unchanged at [B] up to 10%, while shifted to higher energies at higher [B], indicating that optical band gap ($E_g$) increases with [B] from 10 to 18% for the crystalline ZnO:B phase, and the amorphous ZnO:B with [B] = 26% has further larger $E_g$. Optical band gaps were determined by $\alpha h\nu - h\nu$ plots as shown in Fig. 4(b), where the $E_g$ values were determined by extrapolating the straight line regions to $\alpha h\nu = 0$. The $E_g$ of the ZnO:B films with [B] = 0–4% were determined to be 3.25 eV, which agree with the reported value, while increased to 3.45 eV at [B] = 18%. For the amorphous ZnO:B film with [B] = 26%, $E_g$ was determined by Tauc’s plot with the form $(\alpha h\nu)^{1/2}$ ($r = 2$) as shown in Fig. 2(c), giving the $E_g$ value of 3.38 eV. Figure 4(d) summarizes the variation of the optical $E_g$ values obtained by the $(\alpha h\nu)^{3/2}$ plots (direct transition model) and $(\alpha h\nu)^{1/2}$–$h\nu$ plots (indirect transition/Tauc model).

3.4 Electrical properties

Figure 5 shows the electrical properties including $\sigma$, $N_e$, and $\mu_{Hall}$ as a function of [B] in the ZnO:B films depositing at $P_{O_2}$ = 1, 3, and 5 Pa. It was confirmed that all the ZnO:B films with [B] = 26% were amorphous, and the others were polycrystalline. For the ZnO:B films deposited at $P_{O_2}$ = 1 Pa, the polycrystalline films ([B] $\leq$ 18%) have high $\sigma$ $\sim$ 10$^{-2}$ S cm$^{-1}$, $N_e$ $\sim$ 10$^{20}$ cm$^{-3}$, and $\mu_{Hall}$ $\sim$ 10 cm$^2$(V·s)$^{-1}$. With further increasing to [B] = 26%, $\sigma$ and $N_e$ dramatically decreased by 5 order of magnitudes, and $\mu_{Hall}$ also decreased to $\sim$ 1 cm$^2$(V·s)$^{-1}$. The sharp drop in $N_e$ upon amorphization indicates that the amorphous ZnO:B would have electron traps due to defects originating from the disordered structure similar to the a-Si case. The ZnO:B films deposited at higher $P_{O_2}$ show the different behavior. We can see that the $P_{O_2}$ = 3 Pa films shows lower $\sigma$ $\sim$ 10$^{-2}$ S cm$^{-1}$ and $N_e$ $\sim$ 10$^{17}$ cm$^{-3}$ than those of the $P_{O_2}$ = 1 Pa films, which would be understood that stronger oxidation atmosphere compensate the free electrons generated from B$^{3+}$ doping at the Zn$^{2+}$ site.
4. Conclusion

In summary, we investigated growth, structure, and properties of ZnO:B films at room temperature by PLD. The crystalline structure of ZnO is stable for B doping, and amorphous films were obtained only when $[\text{B}]$ increased to 26%. The amorphization reduced the film density from 5.61 to 5.11 g·cm$^{-3}$, which is explained mainly by the incorporation of the light B atoms. The amorphous ZnO:B has larger band gap ($\sim$3.38 eV), smaller $N_e$ ($\sim$10$^{15}$ cm$^{-3}$), and smaller $\mu_{\text{Hall}}$ ($\sim$1 cm$^2$(V·s)$^{-1}$) compared with those of crystalline ZnO.

Reference