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Extended wide band gap amorphous aluminium-doped zinc oxide thin films grown at liquid nitrogen temperature

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Abstract
Amorphous aluminium-doped zinc oxide (AZO) thin films are grown by standard RF sputtering at low temperatures on glass substrates. Due to poor thermal conductivity and thermal energy generated by the sputter gun, controlling the substrate surface temperature is the key to controlling the growth of amorphous and nanocrystalline films. The ratio of grains and amorphous part of the films can be controlled by selective growth conditions. During a transmission electron microscope (TEM) inspection process, the amorphous films react immediately and strongly with an electron beam and transform to a mixture of amorphous and nanocrystalline phases. The films having a mixture of amorphous and nanocrystalline phases, either as-grown or after transformation by irradiation of the electron beam, are stable in the TEM inspection, indicating that the low interface energy stabilizes the mixture phase. The optical band gap increases with the content of amorphous phase and is 4.3 eV for pure amorphous AZO films.

1. Introduction
Transparent conducting oxide (TCO) [1] films have been widely used in optoelectronic devices such as indium tin oxide (ITO) [2, 3], fluorine- and aluminium-doped zinc oxide (AZO : F) [4, 5] and fluorine-doped indium tin oxide (ITO : F) in touch panels and solar cells [2, 6, 7]. For next-generation optoelectronics, flexibility is the basic requirement. ITO and aluminium-doped zinc oxide (AZO) are now coated on nonflexible glass substrates and are polycrystalline [8]. When they are used on flexible substrates, the polycrystalline film suffers severe degradation due to fragmentation by repeated bending [8]. The best solution is to grow an amorphous film instead of polycrystalline films; for instance, the In–Ga–Zn–O film is an amorphous film that exhibits a high level of both transparency and electrical conductivity [9, 10]. The disadvantage of In–Ga–Zn–O is the limited natural resources of In and Ga. Therefore, a high priority exists for amorphous films free from In and Ga content that preserve the high level of transparency and conductivity. Because AZO has been widely used in solar panels [11] and both Al and Zn are abundant, the aim of this study is to develop a growth mechanism for growing amorphous AZO films. However, although it is easy to grow textured ZnO films or polycrystalline AZO films at room temperature, to deposit an amorphous AZO thin film is a great challenge. In this study, a low-temperature (lower than room temperature) technique is used to achieve this goal. It is found that highly amorphous AZO thin films can be deposited on glass and PET by controlling the sputtering power, gas pressure and the sputtering sequences. The emergence of amorphous phase in films can be identified by optical transmittance spectrum, grazing angle incident x-ray diffraction (GIXRD) and transmission electron microscopy (TEM) measurements. The amorphous structure reduces the lattice ordering that enhances quantum size effect and gives rise to higher transmittance and to expanded optical band gap of AZO films from the bulk value 3.4–4.3 eV.
2. Experiment

Amorphous AZO thin films are deposited in a standard RF on-axis sputtering configuration while maintaining the substrate temperature around 77 K. To prevent the condensation of working gas on the substrate due to such low temperatures, high-purity neon gas is used rather than argon or oxygen because its boiling point (27 K) is lower than the liquid nitrogen temperature. The Zn0.98Al0.02O (AZO-2%) target is prepared from high-purity ZnO (99.999%) and Al2O3 (99.997%) powders and sintered at 1400 °C several times for 12 h with flowing oxygen until the density of AZO-2% reaches 75%. The substrates used are Superfrost microscope slides which are made of low-iron white glass and are cleaned in an ultrasonic bath filled sequentially with distilled water, acetone, methanol (10 min each step) and isopropyl alcohol (15 min). A specially designed low-temperature sample holder capable of containing liquid nitrogen cools the substrate to nearly 77 K. Due to the poor thermal conductivity of glass substrates, a certain temperature difference between the substrate and the sputtering gun and the time of deposition is dependent on the sputtering power, distance between the substrate and the sputtering gun and the time of deposition. Water vapour is removed by subsequently pumping the chamber down to 10−6 Torr and refilling with Ne gas up to 1 Torr, a process repeated several times. The sample holder is cooled slowly by pumped-in liquid nitrogen. Once the holder temperature becomes below 0 °C, residual water vapour in the chamber will quickly condense on the sample holder where it is not covered by glass substrates. The background pressure of the chamber is below 2 × 10−6 Torr. During deposition, the Ne pressures in the chamber are set to 5–150 mTorr and various RF powers of 50–300 W are used. The crystal structure, surface morphology and optical transmittance of the films are examined by a four-axis Bede D1 x-ray diffractometer (XRD), a JEOL JEM-3010 analytical scanning transmission electron microscope (TEM), energy dispersion spectrum (EDX), a Digital Instrument NanoMan NS4 atomic force microscope (AFM) and an N&K analyser. The composition of the films is measured by EDX and is found to have Al/Zn ratios distributed within 0.5–1%.

3. Result and discussion

To ensure that the surface temperature of the substrates during growth is as close to the liquid nitrogen temperature as possible, various growth sequences were employed. The growth intervals (on-stage) were varied from 1 to 3 min followed by a period of time (off-stage) during which the shutter of the sputter guns was closed, effectively cutting off the thermal transport from the gun to the substrate. This two-step process was repeated using the same on-stage interval for each subsequence until the total growth time was reached. Various sequences reflect different surface temperatures and mobilities of adatoms on the surface of the films. In the first test the RF power, chamber pressure and total growth time were set at 300 W, 10 mTorr and 15 min, respectively. The thicknesses and optical transmittance spectra of the films grown in various growth sequences are shown in figure 1. The optical transmittance spectra are measured in the unpolarized optical spectrometer (N&K Technology, Inc.) from 190 to 1000 nm with a spectral resolution of 1 nm. It is found that these films have nearly the same thickness, for they are all grown within the same total time. The transmittance of the (G5S2) film is lower than 40% which can be attributed to the huge thermal energy accumulated on the surface of the substrate in the 5 min on-stages and cannot be dissipated efficiently in the 2 min off-stage, therefore, it enhances the growth of sub-micrometre-sized crystals, as shown in figure 2(a). By simply decreasing the on-stage interval, the optical transmittances of (G2S2), (G1S1) and (G3S5) films are improved dramatically. To minimize the possible contamination during the off-stage, fewer two-step processes during growth are used.

The film (G3S5) grown at an on-stage of 3 min and off-stage of 5 min exhibits the highest transmittance, ~90% at 650 nm, of all films and has a very similar band gap to that of the (G1S1) film. Because the transmittance spectra in some cases (in the next few paragraphs) are composed of two overlapped spectra, we define the energy gap to be calculated from the wavelengths at the point of largest slope in the rising stage. All films in figure 1 exhibit a single transition at around 360 nm that corresponds to a band gap of 3.3–3.4 eV. The surface morphology of these films were taken by an AFM in tapping mode, as shown in figure 2. Obviously, the (G5S2) film with the longest on-stage interval is flaked, similar to large crystals, while the others appear more like small grains. The grazing incident angle XRD (GIXRD) patterns taken at 0.5° incident angle, 0.005° step size and 3 s counting time are used to examine the crystal structure of the films, as shown in figure 3. For reference, Miller indices of wurtzite ZnO are listed on the top panel of figure 3. It is obvious that all films
Figure 2. Surface morphologies of the films measured by an AFM in an area of $5 \times 5 \mu m^2$.

Figure 3. Grazing angle x-ray diffraction patterns of films grown at various growth sequences. The Miller indices shown at the top are the corresponding peaks of the ZnO crystal.

are crystalline films filled with sub-micrometre-sized crystals for they all have wide diffraction peaks. The (G3S5) film has the weakest diffraction peaks indicating a nanocrystalline morphology which is very close to an amorphous one. In the rest of this paper, all growth sequences are set to this mode: a 3 min on-stage followed by a 5 min off-stage.

Having determined the proper growth sequence, RF powers from 100 to 300 W are set while the remaining growth parameters, total growth time $= 15$ min and $P_{Ne} = 10$ mTorr, are kept constant. The RF powers during the growth processes, film thicknesses and optical transmittance of the films are listed and plotted in figure 4. The thicker films are grown with a higher RF sputter power, transferring more material from the target to the substrates. The transmittance of each film has a weak correlation with film thickness, $t$; for example, the films grown at 300 W ($t \sim 570$ nm) and 100 W ($t \sim 220$ nm) have similar transmittance ($\sim 91\%$) at around 830 nm. The main transition in transmittance curves, indicated by a dashed box in figure 4(b), is found to shift to the shorter wavelength region, or to a wider band gap, by reducing the RF power. It is interesting to note that in the shorter wavelength region in figure 4(b), nonzero tails appear for films grown at lower powers. This tail emerges at the absorption edge, 250 nm, of glass substrates, and their intensities increase by lowering the RF power. This tailing effect strongly implies that a small portion of amorphous AZO (will be proved by TEM investigation in the following paragraph) is grown simultaneously with the nanocrystalline AZO films. Therefore, the transition point at the tail to the main transition can be defined as the relative percentage of amorphous phase of the film. Obviously, the 100 W RF power exhibits the highest percentage of amorphous phase. Figure 5 shows the surface morphology of these films. Most of them have a similar small grain morphology except for the 300 W film, which shows a mixture of flake-like large crystals and small grains, indicating that the high thermal energy accumulated on the surface of the substrate due to the high RF sputtering power during on-stages enhances the growth of larger crystals. These broad peaks in figure 6 correspond to the major nanocrystal phase of the films.
Since the total growth pressure strongly affects the plasma density and the mean free path of sputtered particles during growth, it therefore affects the sputtering yield and the kinetic energy of sputtered particles on the surface of the substrate. As shown in figures 7–9, these films are grown at various total pressures (5–150 mTorr) of Ne while the total growth time and the RF power are set at 15 min and 100 W, respectively. The film thicknesses vary from 140 to 260 nm with a maximum thickness around 50 mTorr. The optical transmittance measurement, figure 7(b), indicates that the band gap expanded quickly by increasing the growth pressure, finally becoming larger than the band gap, 4 eV, of the glass substrates. The height of the tail, which indicates the percentage of amorphous phase, increases with total pressure. The total pressure of 50–70 mTorr can be regarded as the transition pressure between a mixed phase (amorphous-nanocrystalline) and a pure amorphous phase because the ratio of tails depends randomly on the pressure. When the total pressure is above 100 mTorr, only one transition can be observed, which indicates the growth of the amorphous AZO phase. The surface morphologies and the GIXRD of the films grown at various Ne pressures are shown in figure 8 and 9, respectively. The ZnO peaks become weaker as the Ne pressure increases. For the films grown at Ne pressure higher than 70 mTorr, no identified peaks for ZnO can be observed and only the broad peak from the glass substrates extending from 20° to 40° can be observed. For Ne pressures higher than 150 mTorr, the grown amorphous AZO films are very loosely attached to the glass, and can be easily scratched off by a fingernail.

The lack of observed peaks in GIXRD is not a sufficient indicator of the amorphous phase; the crystal structures of the films are therefore additionally examined by a TEM operated at 120 keV with the smallest aperture and the weakest current to prevent films from damage. The TEM samples were prepared by a dual focus ion beam, SEIKO SMI 3050, and a Pt layer was predeposited as a protection layer. Figure 10 shows the TEM diffraction patterns in (a)–(c), white field image in (d), and high-resolution images in (e) and (f) of a film grown at 5 mTorr, 100 W for 15 min. As described previously, it is mainly composed of nanocrystals with a very small amorphous portion. Figures 10(a)–(c) represent the diffraction patterns taken at different times, Δt of around 40–60 s, which clearly show the same polycrystalline diffraction patterns, indicating...
that the crystal structure is stable over time. Figure 10(d) is the white image of the cross section of the film. Both large columnar crystals across the film from the substrate to the surface of the film as well as multi-grains are observed in a very complicated arrangement. Crystal sizes ranging from a few tens of nm to around 5 nm are estimated from figures 10(e) and (f). In between the grains and columnar crystals, a very small amount of amorphous material can also be observed. For the film grown at 150 mTorr, which has no identifiable diffraction peaks and which exhibits a very high optical band gap, the amorphous state is very unstable. As shown in figure 11(a), its TEM diffraction patterns at the beginning, \( t = t_0 \sim 0 \) s, show very broad peaks that can be identified as an amorphous phase. A few seconds later, \( \Delta t \sim 40–60 \) s and shown in figure 11(b), an obvious diffraction pattern appears and becomes more intensive over the following \( \Delta t \) period, as shown in figure 11(c). Unfortunately, the high-resolution image at the very beginning of the TEM inspection is not available because the films continuously change and crystallize as long as the electron beam is incident on the sample. Only after a few minutes of observation, when the evolution of films stops, can clear high-resolution images from different areas be taken, as shown in figures 11(d)–(f). During the final stage, the film transforms to a film composed of nanocrystals with an average size of \( \leq 5 \) nm. This instability proves that the film was initially amorphous and can be changed to a nanocrystal film simply by irradiation with an electron beam. This also shows that growing amorphous ZnO films with a very low doping level is a great challenge.

X-ray absorption spectra show that the distance of Zn–O decreases slightly and the intensity of Zn–Zn coupling is suppressed dramatically when the Ne pressure is above 70 mTorr. Doping of Al in amorphous ZnO leads to a large deformation of the Zn–O bond and the formation of the amorphous phase under the assistance of the low-temperature growth process. This large deformation reduces the long-range lattice ordering and gives rise to an obvious increase in the valence and conduction band edges. The conduction band edge exhibits a stronger shift than the valence band. The overall band gap is then expanded to 4.3 eV. The expansion of optical band gap can be contributed by the nanosized grains or the amorphous matrix. For those grains of sizes smaller than 5 nm, their quantum size effect can be evaluated by the spherical quantum confinement model proposed by Kayanuma [12]. Tan et al [13] estimated the optical band gap of a 2 nm ZnO nanosphere to be 3.7 eV which is much smaller than the present measured optical band gap, 4.3 eV. Optical transmittance measurements are found to contain two obvious transitions: the tail and main transitions. The amorphous films have only one tail transition and a band gap of 4.3 eV. Those films with nanocrystal inclusions show two transitions.

Figure 8. Surface morphologies of the films measured by an AFM in an area of \( 5 \times 5 \) µm².

Figure 9. Grazing angle x-ray diffraction patterns of the films grown at various Ne pressures.
Figure 10. TEM diffraction patterns, (a)–(c), white field image, (d), and high-resolution images, (e)–(f), of the film grown at 5 mTorr Ne pressure. Each $\Delta t$ is around 40–60 s and $t_0 \sim 0$ s.

in which the tail transition is similar to what is observed in the amorphous films so that one may conclude that the tail transition can be directly assigned to be the contribution of the amorphous part and the very smaller grains with sizes smaller than 2 nm. Meanwhile, the main transition can be attributed to those large nanocrystal inclusions. It is noted that the amorphous phase is not constructed by a complete random distribution of atoms but rather by a structure with very short-range lattice ordering in which the electron wave functions are confined. This situation can also resemble a
simplified spherical model \cite{12} with an ordering length as small as 1 nm \cite{13}.

4. Conclusion

This study deals with the growth of amorphous AZO films with nanocrystalline inclusions at low temperatures. To control the growth of amorphous films, controlling the surface temperature of the substrates during growth is crucial. A medium RF power, short growth time and high Ne pressure are the key parameters for growing amorphous AZO films. The pure amorphous films react immediately with an electron beam during TEM inspection and transform to a mixture of amorphous and nanocrystalline phases. The films composed of a mixture of amorphous and nanocrystalline phases, no matter whether this mixture is formed during the film growth or transformed from a pure amorphous film by irradiating a high-energy electron beam, are stable in TEM inspection indicating that the low interface energy stabilizes the mixture phase. The sizes of nanocrystals in the films vary from a few to a several tens of nanometres. The band gap of AZO is around 3.4 eV for the long-range-order crystalline AZO and it expands to 4.3 eV for the amorphous AZO films.

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