Journal of the Korean Institute of Illuminating and Electrical Installation Engineers Vol. 22, No.11, pp. 36~43 November 2008 (22-11-6)

Electrical Properties of ZnO:Al Transparent Conducting Thin Films for Film-Typed Dye Sensitized Solar Cell

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Abstract

In this paper aluminium-doped zinc oxide(ZnO:Al) conducting layer was deposited on polyethylene terephthalate(PET) substrate by r. f. magnetron sputtering method. The effects of gas pressure and r. f. sputtering power on the structural and electrical properties of ZnO:Al thin film were investigated experimentally. Especially the effect of position of PET substrate on the electrical properties of the film was studied and fixed to improve the electrical properties and also to increase the deposition rate. The results show that the structural and electrical properties of ZnO:Al thin film were strongly influenced by the gas pressure and sputtering power. The minimum resistivity of 1.1×10^{-3}[Ω-cm] was obtained at 5[mTorr] of gas pressure, and 180[W] of sputtering power. The deposition rate of ZnO:Al film at 5[mTorr] of gas pressure was 248[nm/min]. and is higher by around 3 times compared to that at 25[mTorr].

Key Words : Transparent Conducting Layer, PET Substrate, Electrical Resistivity, Optical Transmittance, Magnetron Sputtering

1. Introduction

Recently, deep interest has been paid in using plastic materials for replacing glass substrates with increasing applications for large scale flexible flat panel display and flexible film-typed dye sensitized solar cell(DSCs). In particular, flexible film-typed DSCs have attracted much interest because it can be applied to a smart window, a wearable PC as a supplementary power supplier and a winter clothes[1].

Aluminium doped zinc oxide(ZnO:Al) thin film has emerged as one of the most promising transparent conducting films due to its high electrical conductivity and high transmittance as well as high chemical and mechanical stability, high resistance for deoxidation, and its abundance in nature[2, 3]. ZnO is a Ⅱ-Ⅵ n-type semiconductor with a wide band gap of approximately 3.3[eV] at room temperature and a hexagonal wurtzite structure. The pure ZnO films are highly transparent in the visible range and have low electrical conductivity. However this poor electrical properties can be improved by control of both stoichiometry and donor-like impurities.

When using plastic materials as a substrate

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Date of submit : 2008. 9. 8
First assessment : 2008. 9. 22
Completion of assessment : 2008. 11. 3

there are some technical limitations which we must overcome, such as lower working temperature and rougher surfaces as compared to glass substrate. That is, in fabricating the ZnO:Al film by dc or r. f. sputtering methods, the substrate heating is considered to be one of the essential processes to obtain the high electrical and optical properties. If, without substrate heating, the film shows an incomplete reaction and rough films are obtained[4]. But with increasing temperature the film becomes nonstoichiometric structure, which produces a decrease in the resistivity due to the oxygen vacancies and interstitial zinc atoms which act as donors, giving improvements in electrical and optical properties. However, in the case of polymer substrate, we cannot use the substrate heating due to the poor thermal resistance of polymer substrate[5]. Moreover, the deposition rate of ZnO:Al film deposited on the polymeric substrate cannot be comparable with that deposited on glass substrate[6]. But the systematic studies on the ZnO:Al transparent conducting film deposited on polymeric substrate cannot be performed.

In this paper in order to investigate the possible application of ZnO:Al film as a transparent conducting oxide(TCO) electrode for DSCs, aluminium doped zinc oxide films were deposited on polyethylene terephthalate(PET) substrate by r. f. magnetron sputtering method. The influences of gas pressure and r. f. discharge power on the structural, electrical and optical properties were studied and discussed.

2. Experimentals

Fig. 1 shows schematic diagram of experimental setup. In order to improve the deposition rate and to protect the PET substrate from direct contact of thermal energy of plasma body, the substrate was placed 6cm apart from the target as shown in Fig. 1. The average distance between target and PET substrate was 60[mm]. ZnO:Al films were prepared on PET(30×30×0.25[mm]) by the conventional r. f. magnetron sputtering. The sputtering target was a mixture of ZnO (99.99[%]) and Al_2O_3(99.99[%]), pressed on a copper saucer with a diameter of 3inch. The PET substrate was

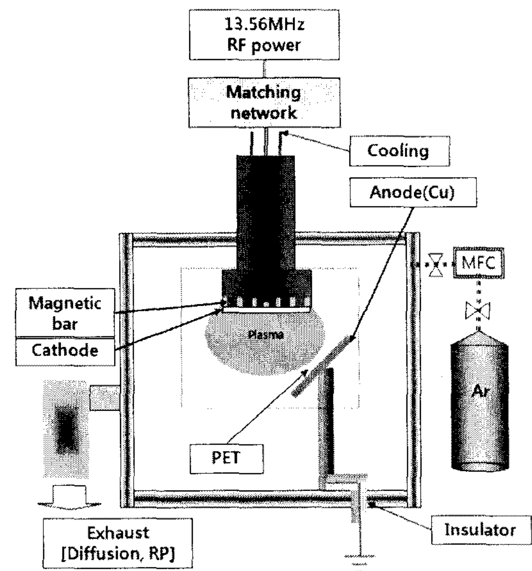


Fig. 1. Schematic diagram of experimental setup

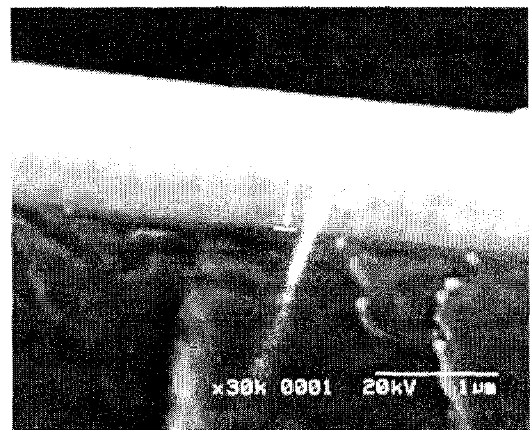


Fig. 2. SEM photograph of ZnO:Al film at the gas pressure of 5[mTorr] and r.f. power of 180[W]

cleaned prior to each deposition in an ultrasonic cleaner, and dried by nitrogen flow. Prior to sputtering, the sputtering chamber was evacuated to a base pressure of 10^{-6}[Torr] and was heated at about 400[℃] for degassing the equipments. To maintain the same target condition for each deposition, the target was also sputtered in pure argon (Ar: 99.999[%]) environment prior to each deposition with the shutter covering the substrate. The Ar gas pressure and discharge power were varied from 1[mTorr] to 25[mTorr] and from 160[W] to 240[W], respectively.

Thickness and sputter yield of the ZnO:Al films were measured at given experimental conditions using DEKTAK 300 alpha-step or were obtained from direct measurements of SEM photographs. Fig. 2 shows typical example of SEM photographs of the sample deposited at the experimental conditions of 180[W] and 5[mTorr]. Crystalline structures of the films were characterized by a Rigaku D/max 2,100[H] X-ray diffractometer (XRD). Surface morphology of the film was studied using atomic force microscopy(AFM). Spectral transmittance was also measured using a Hitachi U 3,000UV-spectrophotometer.

3. Results and Discussions

3.1 Structural Properties

Fig. 3 shows the effect of gas pressure on the X-ray diffraction patterns of ZnO:Al film. As well known in Fig. 3, ZnO:Al films show the (002) preferred orientation regardless of gas pressures, and they are located at 2Θ=34.5[°], which are very close to that of the standard ZnO crystal(34.45[°]). The very weak (004) peaks also appeared at near 2Θ=72[°] up to 10[mTorr]. But (004) peaks were not observed at higher gas pressure. It was also clearly seen in Fig. 3 that (002) peak intensity of the film deposited at 5[mTorr] was the strongest, compared to the films deposited at other gas pressures. However, the (002) peak intensity decreased when the film was deposited at higher gas pressure than 5[mTorr], and the peak decreased significantly from 15[mTorr]. This result could be related to an increase in energy of sputtered atom arriving at the substrate because a decrease in gas pressure makes a mean free path of the sputtered atom long. That is, as gas pressure decreases, the sputtered atoms with energy obtained as a result of interchange with that of positive ion in the plasma can easily arrive at substrate without collision with Ar gas molecule. It is also expected that as gas pressure decreases from 25[mTorr] to 5[mTorr], the energy of electron in the plasma increases due to longer mean free path. This highly energized electron bombards the growing film on substrate, providing thermal energy for the deposited atoms. This increasing energy of electron can be utilized to promote the sputtered atoms to grow in a particular order, resulting in the strong (002) preferred orientation. That is, an appropriate gas pressure induces an improvement in the crystallinity of the film. In this study the optimized condition of gas pressure was 5[mTorr].

Fig. 4 shows the influence of r. f. sputtering power on the X-ray diffraction patterns of ZnO:Al films. In the Fig. 4, the peak intensity increases with increasing sputtering power up to 180[W], and then the intensity of the (002) peak decreases from 200[W] of sputtering power. This can be attributed to the fact that the numbers or energy of electrons and ions in the glow discharge plasma will increase with an increment in sputtering power. That is, the energy of sputtered atom obtained as a result of interchange with that of positive ion in the plasma will increases with increasing discharge power. Thus the energy of

sputtered atom arriving at substrate increases due to the increase in discharge power to 180[W], resulting in the strong (002) preferred orientation. That is, an increase in sputtering power also induces an improvement in the crystallinity of the film. However, the excessive supply of sputtering power over than 180[W] may cause a degradation of the preferred orientation, resulting in the high defect density and small grain size.

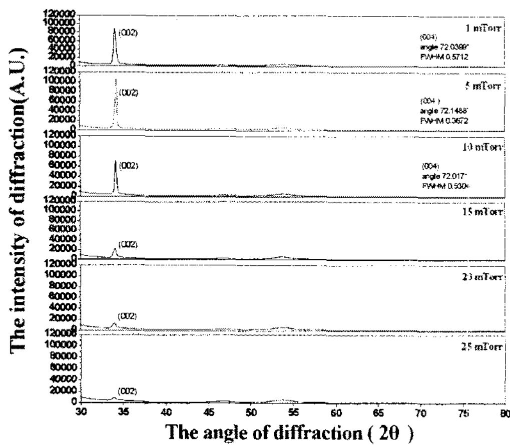


Fig. 3. Effect of gas pressure on the X-ray diffraction patterns of ZnO:Al film

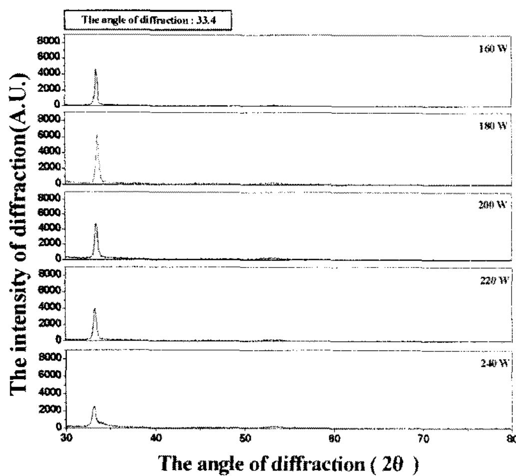
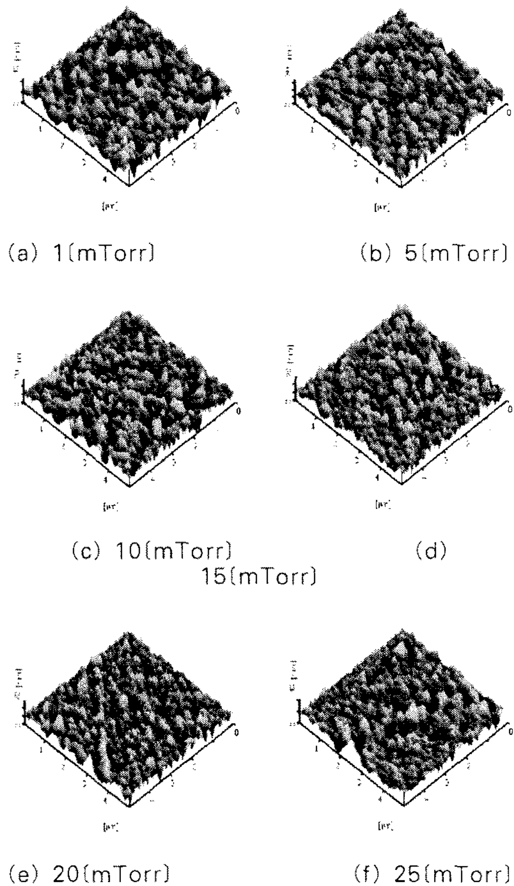


Fig. 4. Effect of sputtering power on the X-ray diffraction patterns of ZnO:Al film

In order to confirm the effect of sputtering power on the morphology of the film, the AFM morphologies of the films deposited at different gas pressures and r. f. powers were investigated. The results are shown in Fig. 5 and Fig. 6, respectively. In the figures, as the r. f. power increases up to 180[W], the crystallinity of the film is improved and crystalline size becomes larger. However, higher r. f. power over than 180[W] is expected to produce compressive stress in the films due to the different thermal expansion coefficient between the film and PET substrate, and then the film shows loose structures and small



(a) 1[mTorr] (b) 5[mTorr]

(c) 10[mTorr] (d) 15[mTorr]

(e) 20[mTorr] (f) 25[mTorr]

Fig. 5. AFM morphologies of the films deposited at different gas pressures

grain sizes. AFM morphology was also influenced by gas pressures. The optimized condition for crystalline growth was at 5[mTorr] of gas pressure, and this result agrees with the XRD result.

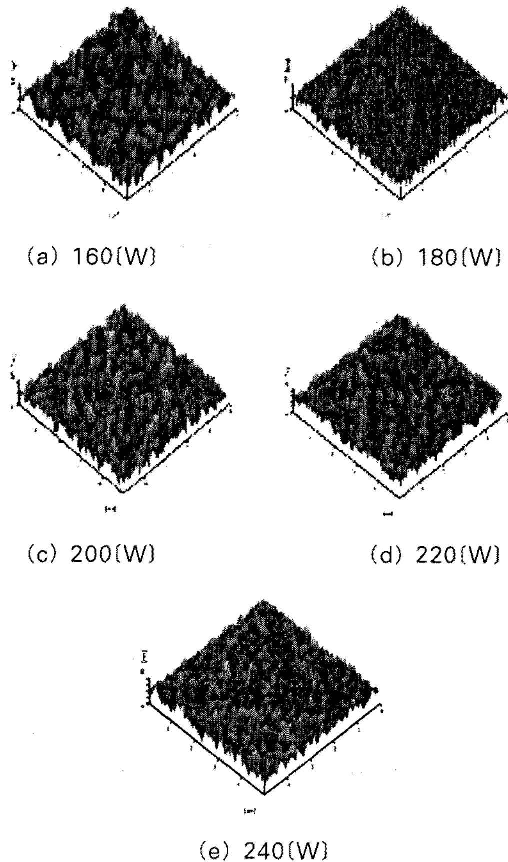


Fig. 6. The AFM of ZnO:Al thin films at working pressure of 5(mTorr) and various r.f. powers

Fig. 7 and Fig. 8 show the full width at half maximum (FWHM) of the (002) peak and the grain size of the film as function of gas pressure and r. f. power. The grain sizes of films were calculated using Scherrer's formular. The FWHM of the (002) peak decreased with increasing r. f. power up to 180[W], and thereafter increased abruptly with increasing sputtering power, which means the peak becomes more intense and sharper up to 180[W] of r. f. power. This results are consistent in that the crystallinity of the film deposited at 180[W] is improved and the crystalline size becomes larger. The largest grain size was also found to be 9.4[nm] for the film at 180[W], and was increased by ~25[%] compared to the film at 240[W].

It is also well known that the grain size at 5[mTorr] at (002) preferred orientation is bigger than those at 1[mTorr] and 10[mTorr]. Although the grain size at 20[mTorr] was the biggest, the

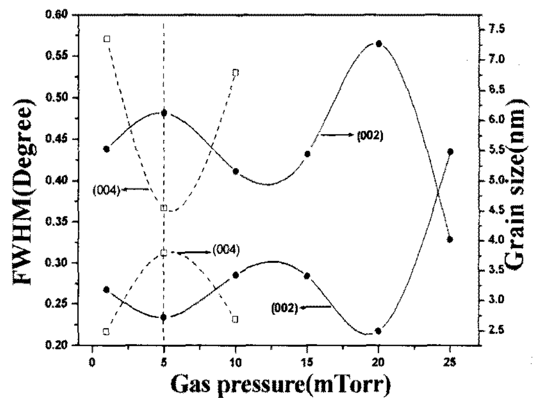


Fig. 7. FWHM of the (002) peak and grain size of the film as function of gas pressures

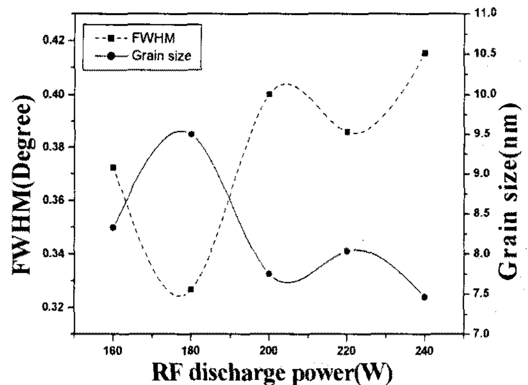


Fig. 8. FWHM and Grain size of ZnO:Al film at gas pressure of 5(mTorr) and various r.f. powers

crystalline grain grew very nonuniformly at 20[mTorr] as shown in Fig. 5. Therefore the XRD peak cannot be strong at this gas pressure condition.

3.2 Electrical Properties

In general, in the case of using polymer substrate, the electrical resistivity and the deposition rate of ZnO:Al film cannot be comparable with those deposited on glass substrate[6]. Therefore, in this study the effect of position of PET substrate on the electrical properties of the film was studied and fixed 6cm apart from the target as shown in Fig. 1. This arrangement of electrode geometry allowed to protect the PET substrate from direct contact of thermal energy of the plasma body, and to improve the electrical properties and deposition rate. In this experiment the film thickness was in the ranges of 1260~1320[nm] in the 160~240[W] of r. f. power ranges, and the average film thickness was 1315[nm]. The surface resisitivity of the 8.2 [Ω]/square was also obtained at 180[W] of r. f. power and 5[mTorr] of Ar gas pressure. These results are comparable with those of ITO, and are considered enough for the film-typed DSCs as a transparent conducting layer.

Fig. 9 illustrates the electrical resistivity and deposition rate of the film at 180[W] and at various gas pressures. The deposition rate was in the ranges of around 85~248[nm/min]. in the gas pressure 1 to 25[mTorr], and increased with increasing gas pressure from 1[mTorr] to 5[mTorr], and decreased abruptly thereafter. The maximum deposition rate of 248[nm/min]. was obtained at 5[mTorr]. This value is higher by around 3 times than that at 25[mTorr], and is comparable with that at using glass substrate. The increase in deposition rate with decreasing gas pressure from 25[mTorr] to 5[mTorr] is attributed to an increase in energy of sputtered atom arriving at the substrate due to the low possibility of scattering of Ar gas molecule. It is also clearly seen from the figure the electrical resistivity increased almost linearly with increasing gas pressure. The minimum resistivity of 1.1×10^{-3}[Ω-cm] was obtained at 5[mTorr] of gas pressure. In the case of aluminium doped zinc oxide, about the effect of gas pressure on the conducting mechanism, the variation in grain size at different gas pressure is considered to be one of the causes which affect the conduction mechanism[7]. In our experiment, as mentioned earlier in Fig. 3, the XRD peaks become more intense and sharper with decreasing gas pressure from 25[mTorr] to 5[mTorr]. Besides the FWHM result with variation in gas pressure in Fig. 7 shows that the FWHM is the lowest at 5[mTorr] of gas pressure. These results reveal that the grain sizes of crystallites increase and grain boundary decreases with decreasing gas pressure to 5[mTorr]. Therefore the improvement of electrical resistivity at 5[mTorr] is ascribed to a decrease in the scattering centre for carriers.

Fig. 10 shows the dependences of electrical resistivity and deposition rate of the ZnO:Al films sputtered at a gas pressure of 5[mTorr] on sputtering power. As the sputtering power increases from 160[W] to 200[W], the deposition rate increases almost linearly from 225[Å/min] to 425[Å/min], and decreases thereafter. The increase in deposition rate with increasing discharge power is attributed to an increase in energy of sputtered atom arriving at the substrate due to the increment of discharge power. It is also clearly seen that the electrical resistivity of the film decreases from 1.75×10^{-3}[Ω-cm] to 1.1×10^{-3}[Ω-cm] as the sputtering power increases from 160[W] to 180[W], and thereafter it increases

abruptly. From the analysis on the mophological properties in Fig. 6 and Fig. 8, which show the dependence of structural properties on the sputtering power, crystalline grain size are improved with increasing sputtering power up to 180[W]. These results reveal that the grain size increases and grain-boundary decreases with increasing sputtering power. Therefore, the improvement in electrical resistivity with increasing discharge power up to 180[W] is ascribed to decrease in the number of scattering centre for carriers, giving a low electrical resistivity. However, the excessive supply of sputtering power limits the growth of crystalline grains due to too high deposition rate (180[W]: 250[Å/min], 200[W]: 425[Å/min].). The increment in r. f. power from 180 to 200[W] increases deposition rate by more than 60[%].

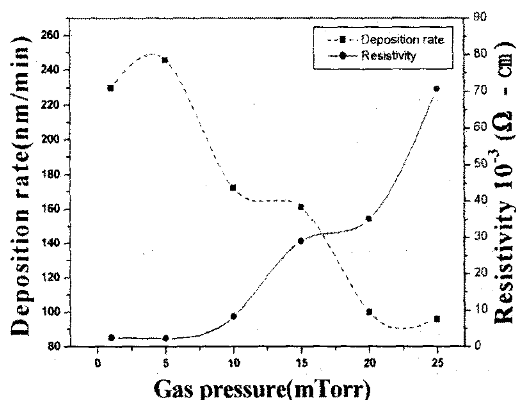


Fig. 9. Electrical resistivity and deposition rate of the film at various gas pressures

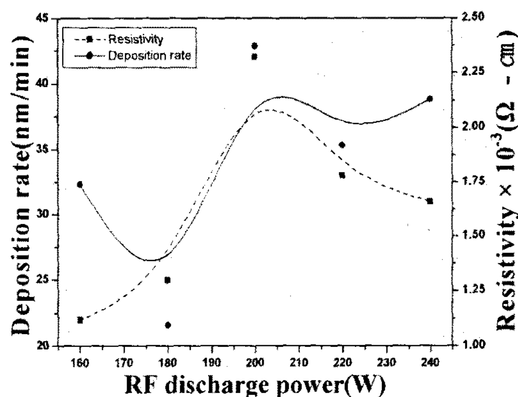


Fig. 10. Electrical resistivity and deposition rate as a function of sputtering power

Fig. 11 illustrates the optical transmittance of the film deposited at various r. f. discharge powers and at 5[mTorr] of gas pressure.

From the figure, the transmittance is found to increase from 84.2[%] to 85.2[%] as discharge power increases from 160[W] to 180[W], and decreases to 79[%] with increasing r. f. power. The average transmittance was over 80[%] in the visible ranges.

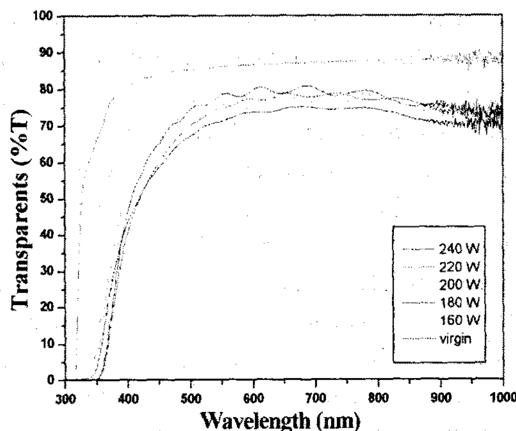


Fig. 11. Transmittance of the film deposited at various r. f. sputtering powers

4. Conclusion

In this paper aluminium-doped zinc oxide (ZnO:Al) conducting layer was deposited on polyethylene terephthalate(PET) substrate by r. f. magnetron sputtering method. The effects of gas pressure and r. f. sputtering power on the structural and electrical properties of ZnO:Al thin film were investigated experimentally. The results show that the resistivity of the film was strongly

influenced by the gas pressure and r. f. sputtering power. The electrical properties were improved with increase in sputtering power and gas pressure up to 180[W] and 5[mTorr]. However excessive supply of sputtering power limits the growth of crystalline grains due to too high deposition rate and may cause a degradation of the preferred orientation, giving high electrical resistivity. The lowest resistivity and optical transmittance were 1.1×10^{-3}[Ω-cm] and 85.2[%], respectively and were obtained under the experimental conditions of 180[W] of sputtering power and 5[mTorr] of gas pressure.

This Research was supported by Kyungsung University Research Grants in 2006.

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Biography

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Dong-Joo Kwak was born in Busan, Korea, in June 1958. He received the master's degree in electrical engineering from Konkuk University, Korea, in 1985, and the Ph. D. degree, in 1989 from Kyushu University, Japan.
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