ULTRA THIN INDIUM TIN OXIDE FILMS ON VARIOUS SUBSTRATES BY PULSED LASER DEPOSITION

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ABSTRACT

Indium Tin Oxide (ITO) thin films with low resistivities of 0.1-0.2 mΩ-cm were deposited on various substrates such as YSZ, glass, and ZnO buffered glass by pulsed laser deposition (PLD). The X-ray rocking curve of crystalline (200) ITO films grown on (100) YSZ had a FWHM as narrow as 0.08°. ITO films grown on ZnO (0001) buffered glass had an single (222) orientation and the X-ray rocking curve had a FWHM of 2.1°. Ultrathin ITO films of 3.6nm were fabricated on YSZ and their electrical properties were measured from 10K-300K. ITO films fabricated on ZnO buffered glass and bare glass were characterized by Hall effect measurements as a function of temperature. The results indicate that the resistivity of ITO films grown by PLD does not depend on the orientation or the structure of the thin film. The resistivity is dominated by impurity scattering in the range of 10K-300K. We show that ZnO/glass is a good alternative to bare glass for producing commercial ITO films.

INTRODUCTION

Tin-doped Indium Oxide (ITO) is an n-type wide band-gap semiconductor. It is widely used in flat panel displays and solar cells due to its unique property of both electrically conductive and optically transparent in the visible region. The low resistivity of ITO film is due to the large free carrier density, which is in the range of 10²⁰/cm³ to 10²¹/cm³. It is generally accepted that these free carriers are generated by two mechanisms: (1) Sn atom substitution of In atom and giving out one extra electron, (2) oxygen vacancies acting as two electron donors [1]. Due to its complicate crystal structure (80 atoms in a In₂O₃ unit cell [2]), the conducting mechanisms of ITO is still not fully understood.

ITO thin films in commercial use are mostly amorphous. There is always some interests in growing crystalline ITO because of scientific curiosity as well as for practical reasons. Attempts have been made to grow well-oriented ITO films without large grain boundaries on MgO and yttrium-stabilized zirconia (YSZ) [3,4,5]. The best crystalline ITO film grown on YSZ has an X-ray rocking curve FWHM of 0.29°. The X-ray rocking curve FWHM of the best ITO films grown on MgO is about 1.5° [3]. In this paper we report ITO films grown on YSZ with an X-ray rocking curve FWHM as narrow as 0.08°, which is the narrowest to our knowledge. This highly crystalline ITO on YSZ should find applications in opto-electronics. As an alternative to crystalline substrates, we also investigated the possibility of obtaining highly textured ITO films on glass. This method involves using ZnO as a buffer layer. ZnO is an interesting material in that it is very easy to make crystalline films of, and it is also transparent and conductive. Therefore it is highly compatible with ITO in commercial production. We shall show that indeed very good quality ITO films can be grown on ZnO/glass.
EXPERIMENTAL

The ITO films were deposited in a conventional turbo-mechanical two stage pumped chamber which can be pumped down to $3 \times 10^{-7}$ Torr. The ITO (99.999%) and ZnO (99.99%) targets used were commercially available hot-pressed and sintered pallets. The substrates were cleaned with dilute HCl solution and acetone. For those ITO samples with ZnO buffer on glass, the ZnO buffer was deposited just before ITO film in the same chamber with the same deposition conditions. The ArF excimer laser (Lambda Physik) was operated at 150mJ per shot at 10Hz repetition rate. At a substrate temperature of 400°C, the optimized deposition parameters for ITO films were 5cm of target-substrate distance and 20mTorr of ambient.

All the samples were analyzed by X-ray diffraction (XRD). The resistivity of ultra-thin as-deposited ITO on YSZ were measured from 10K to 300K. ITO on glass with and without ZnO buffer were compared with each other by Hall effect measurement as a function of temperature from 70K to 300K.

RESULTS AND DISCUSSIONS

The ITO films grown on different substrates have thickness ranging from 3.6nm to 200nm. The ZnO buffer film on glass had a thickness of about 20nm. The thickness of the films were estimated by the deposition rate which was calibrated by a profilometer.

The best crystalline ITO was got by using a YSZ substrate, since the lattice mismatch between (200) ITO and (100) YSZ is only 2% ($a_{\text{In}_2\text{O}_3}=10.118 \approx 2a_{\text{YSZ}}=10.26\AA$) [6]. The X-ray $\theta$-2$\theta$ scan of ITO films grown on (100) YSZ at 400°C under optimized deposition conditions is shown in Fig. 1. Only the (400) peak of indium oxide was observed within the scanning range of 20°–60°. The X-ray rocking curve is also shown in Fig. 1. The FWHM of the (400) peak was found to be as narrow as 0.08°. The small lattice mismatch between YSZ and In$_2$O$_3$ is believed to be the reason for the excellent crystallinity of the ITO film. As shown by Tarsa et al, ITO could heteroepitaxially grow on YSZ(100) with (001)ITO||(001)YSZ, (100)ITO||(100)YSZ by PLD with a FWHM of X-ray rocking curve of 0.29° [3]. These heteroepitaxial ITO films on YSZ with superior crystalline quality make YSZ a strong candidate for the substrate material in electro-optic applications, but with a much higher cost than glass.

To characterize the electrical properties of the crystalline ITO film on YSZ, ultrathin ITO films were deposited and their resistivity measured. Fig. 2 shows the resistivity of ITO ultrathin films deposited on (100) YSZ substrate at a substrate temperature of 400°C for film thickness of 3.6nm, 10.0nm, and 40.0nm, as a function of temperature. The resistivity of a 40nm thick film was only about 0.3m$\Omega$-cm which was very close to the bulk value of 0.1m$\Omega$-cm. This indicates that the 40nm film is already of very good quality. It can also be seen that the resistivity of the ITO film increases as the film thickness decreases. The relatively large resistivity of thinner film can be due to two main reasons: film thickness fluctuations and surface scattering. Film thickness fluctuations originate from island growth of ITO film. While the film thickness estimated from the deposition rate represents the average film thickness, the resistance of ultrathin films is determined by the links between the islands. Therefore, film thickness fluctuations become more severe with thinner films. For example, the calculated resistivity value can be differ as much as 50% for 3.6nm thick film with one monolayer fluctuation for Frank-van der Merwe growth mechanism [7]. Notice that 3.6nm is just the thickness of three unit cells. A contribution from surface scattering can also give a larger resistivity value for thinner film. When the film thickness is smaller than the mean free path of free carriers, surface scattering will enhance film resistivity greatly.
From Fig. 2, it can be seen that the resistivity changes very little within the temperature range of 10K to 300K, which indicates the highly degenerated nature of ITO. Two different trends in resistivity-temperature (R-T) curves were also observed as the thickness of the thin film changed. For the 3.6nm thick sample, the resistivity increased slightly with the decreasing of temperature. While the resistivity showed a slight decrease with decreasing temperature for the 10.0nm and 40.0nm samples. The positive R-T slope of thick films of 10.0nm and 40.0nm can be explained by a larger increase in mobility and smaller decrease in carrier concentration with decreasing temperature, because of the degeneracy at lower temperatures. Relatively larger thickness fluctuations for the thinner films may provide an explanation for the negative R-T relationship. Large surface fluctuations can cause sufficient disturbances in the local potential energy for localization of electron wave function. Localized system has an negative R-T slope due to Anderson transition [8].

For ITO films grown on glass and on ZnO buffered glass, their crystal structures and electrical properties will be discussed together for convenience of comparison. The X-ray θ-2θ scan of ITO on glass and on ZnO buffered glass were depicted in Fig. 3(a) and Fig. 3(b) respectively. The ITO film on bare glass is necessarily polycrystalline. It shows three preferred orientations of (211), (222), and (622), indicating a mixed orientation. But for ITO on ZnO buffered glass, the film shows only the (222) orientation, including a (444) peak, in the scan range of 20° to 80°. Notice that Fig. 3(a) has a linear scale while Fig. 3(b) has a log scale. The intensity of the X-ray peaks for the ZnO buffered case is much stronger than that on bare glass. This is very obvious because of the near lattice matching condition for the former case. ZnO has also been used before as a buffer to grow GaN films [9], due to its small lattice mismatch and ease of growth. For ITO grown on ZnO, Yi et al proposed a packing model of (111) In$_2$O$_3$ on (0001) ZnO by calculating the O-O atomic distances on the closest packed planes [10]. The mismatch between the O-O distance of (111) plane of In$_2$O$_3$ and the O-O distance of (0001) plane of ZnO is just about 3%. The X-ray rocking curve of the as-grown ITO film on ZnO buffered glass is inserted in Fig. 3(b). The FWHM of the rocking curve is 2.1°, which is comparable to the ITO films grown on MgO [3], but much wider than that grown on YSZ. Apparently, the 2% vs 3%
lattice mismatch, and the orientation of the lattice matching condition, make a big difference in the crystallinity of ITO.

Fig. 3(a) X-ray θ-2θ data of ITO grown on glass at substrate temperature of 400°C.

Fig. 3(b) X-ray θ-2θ data of ITO grown on ZnO buffered glass at substrate temperature of 400°C. The X-ray rocking curve of ZnO (0002) is also shown.

Temperature dependent Hall effect measurements were also performed on the ITO grown on glass with/without the ZnO buffer. The mobility, carrier concentration and resistivity were given as a function of temperature in Fig. 4(a), (b), and (c) respectively, with the solid dots representing ITO grown on glass and the opened circles representing ITO grown on ZnO buffered glass. In both cases, the carrier concentration is almost constant throughout the scanning temperature range of 70K to 300K, which indicates the highly degenerate nature of ITO. The carrier concentration of ITO grown on bare glass is about $1.45 \times 10^{21}$ cm$^{-3}$ which is slightly larger than the ITO grown on ZnO buffered glass ($1.25 \times 10^{21}$ cm$^{-3}$). The decrease in carrier concentration may be due to the more crystalline structure of ITO grown on ZnO buffered glass, since this will decrease the defect density, resulting in a decrease of donor concentration. This result seems contradictory with that of Taga et al [6]. Their result by e-beam evaporation indicated that more crystalline structure will enhance the solubility of Sn in In$_2$O$_3$ matrix. But it should be noted that the carrier concentration of ITO films on glass by e-beam evaporation is in the range of $10^{20}$/cm$^3$. While the carrier concentration of ITO on glass by PLD is in the range of $10^{21}$/cm$^3$, which is reaching the solubility limit [1]. Under such circumstances, an increase in the crystalline structure will mainly lower the defect density.

The mobility of the ITO grown on ZnO buffered glass (35cm$^2$/V-s) is larger than that of ITO grown on glass (24cm$^2$/V-s), as it is expected from the more crystalline structure. Under both substrate conditions, the mobility showed a slight decrease with increasing temperature in the range of 70K to 300K due to phonon scattering. The resistivity of ITO films followed the reciprocal trends of mobility in the scanning temperature range. The resistivity of ITO films followed the reciprocal trends of mobility in the scanning temperature range. The resistivity of ITO grown on ZnO buffered glass is about 0.155mΩ-cm and 0.19mΩ-cm for ITO grown on bare glass for 150nm films. These values are among the smallest values of ITO thin films. The resistivity is not that sensitive to the crystal quality as observed by Taga et al [6]. The resistivity of the PLD ITO
films are much lower, probably due to the presence of energetic particles and surface activation in PLD [11].

The resistivity of ITO grown YSZ, ZnO buffered glass, and bare glass under optimized conditions by PLD have comparable values, indicating that the resistivity of ITO film is not sensitive to the substrate materials by PLD. Additionally, the resistivity of these films is almost constant in a wide temperature range. This indicates that neither phonon scattering nor grain boundary scattering has a dominating effect on resistivity. For PLD ITO films, and for ITO films in general, the resistivity is mainly determined by the ionized impurity scattering.

![Graphs showing Mobility, Carrier Concentration, and Resistivity vs Temperature](image)

**Fig. 4** (a) Mobility, (b) Carrier concentration, and (c) Resistivity of ITO films grown at 400°C on glass (solid dot) and ZnO buffered glass (opened circle) as a function of temperature.
CONCLUSIONS

In summary, we have fabricated near-epitaxial ITO on YSZ, highly textured ITO on ZnO buffered glass, and polycrystalline ITO on glass. The resistivity of ITO films grown on these three different substrates is in the range of 0.1~0.2 mΩ-cm. The resistivity is not sensitive to the crystal structure by PLD due to two interacting mechanisms during film growth: defect formation by energetic particles in the plasma and increasing solubility of Sn in In₂O₃. The resulting resistivity is mainly determined by impurity scattering in the temperature range of 10K-300K.

YSZ, ZnO buffered glass and glass substrates present different choices of substrates for ITO films. YSZ substrate is a good choice for heteroepitaxially ITO growth, but is quite costly. Bare glass is cheap and is a common substrate for commercial ITO films. However, it can be seen that the quality of the ITO film improves greatly if ZnO buffered glass is used. Both the crystallinity and the ITO resistivity are much better. It is a much better substrate for the growth of ITO films, considering the performance to cost ratio. Since good quality ZnO can be deposited at 400°C by sputtering, it is believed that ITO/ZnO/glass can find good opportunities in commercial applications.

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REFERENCES