Effect of substrate feature on surface morphologies and properties of ITO films deposited by RF magnetron sputtering

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Abstract. ITO films were deposited on c-Si wafer, and two glass substrates by RF magnetron sputtering at constant RF power, and substrate temperature of 60 W, and 450°C respectively. The surface morphologies of the substrates were analyzed before and after film depositions by AFM measurements. The crystalline structural, electrical, and optical properties were analyzed after film depositions by XRD, Hall measurement, and UV-Vis spectrophotometer respectively. It was found that, with lower surface roughness, the deposited ITO films showed significant larger domain-grain structure, lower surface roughness, and higher (400) preferred orientation than that deposited on the substrate with higher surface roughness, with the transmittances of higher than 80% for both substrates. From the structural, and electrical properties, it implied that, with higher surface roughness, the carrier concentrations was contributed mainly from the Sn substitution, whereas it was dominant from the oxygen deficiency for the lower surface roughness substrate. The deposited ITO film with lower resistivity and high transmittance can be achieved for the films deposited on lower substrate surface roughness.

1. Introduction

Indium Tin Oxide or ITO is an n-type degenerated semiconductor, and widely used as transparent electrode thin film in various applications [1-4] because of unique properties of high transmission in visible region (> 80%) and lower electrical resistivity (~10^-4 Ω.cm). The ITO films can be prepared by various methods including RF magnetron sputtering [5-10]. The RF magnetron sputtering has been used to prepare the ITO films with low resistivity, high transparency, and good uniformity on large area. The low electrical resistivities of the ITO films result from non-stoichiometry produced by Sn substitution, and oxygen vacancy in the bixbyte structure [11], which donate one, and two electrons respectively for conductions. However, it is well known that the electrical and optical properties of the ITO film are inversely proportional, and also relate to the film structure characteristics. It was reported that oxygen deficiency leads to films oriented in the <100> direction, whereas the ITO coated films with the stoichiometric structure prefers in <111> direction [9,13]. Various deposition parameters such as RF power, and substrate temperature normally have been used to investigate the competition of such two mechanisms during film depositions. These parameters directly affect to the mobility of
deposited adatom, corresponding to energy of adatom, on the substrate surface, which has an impact on the modification of the preferential orientation growth from <111> to <100> direction [12-16]. Additionally, effects of substrate nature on crystalline structure, electrical, and optical properties have also been reported [17,18]. However, the effects of substrate natures, in spite of their differences of surface roughness, have not been reported clearly.

2. Experimental details

The ITO films were prepared by home-built RF magnetron sputtering system operating at 13.56 MHz via an auto-tuning matching network on 25 x 15 mm² two glass substrates, named as glass A and B, and c-Si wafer at substrate temperatures of 450°C in order to study effect of substrate feature on morphology electrical and optical properties of deposited ITO films. ITO target used in this study is 2 inches diameter ceramic target which composes of 90 wt.% of In₂O₃ and 10 wt% of SnO₂ (Kurt J. Lesker Co., Ltd.). The glass substrates were cleaned by steeping into acetone and methanol of ultrasonic bath for 10 minutes before using nitrogen to blow dry. Before and after film depositions, surface morphologies of the substrates were measured the by using atomic force microscope (AFM) (SPI3800N, Seiko Instrument Inc.) in contact mode. In sputtering process, the glass slides were placed into the chamber at the distance of 9 cm away from the ITO target. The chamber was evacuated to the base pressure less than 2.0x10⁻⁶ mbar by a set of a rotary pump, liquid nitrogen cooling trap, and a turbo molecular pump. High-purity argon gas (99.995%) was fed into the chamber up to the working pressure at 2.0x10⁻³ mbar. The glass substrates were deposited at a constant RF-power of 60 W. The deposition time was kept constant at 7 minutes corresponding to calibrated film thickness about 100 nm determined by surface profilometer (Dektak 3 ST Surface Profile Measuring System, Sloan Tech.). The deposited ITO films were then characterized for crystalline structure, and electrical-optical properties by X-ray diffraction technique with Cu-Kα radiation (D8 diffractometer, Bruker), Hall measurement (HMS-3000, Ecopia) and UV-visible spectrophotometer (HP-8452A diode array spectrophotometer, Hewlett Packard) respectively.

3. Results and discussion

AFM images of 5 x 5 μm² c-Si wafer, and two glass substrates as referred to glass A and glass B, are shown in Figs. 1(a) - (c) respectively. The three substrates show different surface morphologies obviously. It can be noticed that the c-Si wafer shows much smoother and more uniform surface than the glass substrates. Accordingly, average surface roughness, determined from the AFM measurements, are 0.14, 0.56, and 2.83 nm for the c-Si wafer, glass A, and glass B respectively, as shown in Table 1. AFM images, and XRD spectra of the ITO films coated on the c-Si wafer, and both glass substrates are shown in Figs. 2, and 3 respectively. From the Fig. 2, domain-grain structure of the ITO films deposited on the c-Si wafer and the glass A can be observed whereas it could not be observed for the films deposited on the glass B. Average surface roughness of the ITO films coated on the c-Si wafer, glass A, and glass B are 0.56, 0.86, and 1.54 nm respectively, as shown in the Table 1. From the Fig. 3, it illustrates that preferred orientations of the crystalline structures of the deposited ITO films depend on the substrates. The ITO films deposited on the c-Si wafer have preferred orientation in (400) plane rathen (222), whereas deposited ITO films on the glass A, and B preferred orientation in (222) plane rather than (400) plane. The relative intensity ratio of (222) and (400) planes (I(222)/I(400)) of the deposited ITO films on such three substrates are shown in the Table 1. The I(222)/I(400) ratios determined from integrated areas of the XRD spectra are 0.92, 1.54, and 4.24 for the c-Si wafer, glass A, and B respectively. From the Table 1, it also shows structure properties of the deposited ITO films on such three substrates. Average crystallite sizes of the ITO films coated on all substrates are 20, 27, and 37 nm respectively. These results were determined from full-width at half maximums (FWHMs) of XRD spectra, as shown in Fig. 3. The grain sizes were determined by using the Scherrer’s formula: \( t = \frac{(0.9)\lambda}{B\cos\theta_b} \), where \( t \) is diameter of the crystal, and \( B \) is the FWHM.
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Fig. 1 AFM images of (a) c-Si wafer, (b) glass A and (c) glass B.

The differences of observed surface morphologies, and the XRD spectra may be explained in terms of adatom mobility which occur different stoichiometric for the deposited adatoms on each substrate. It can be noticed that higher mobility of adatom on substrate surface leads to higher preferred orientation in (400) plane, larger domain structure, and smaller grain size. Lower adatom mobility for example glass B, may be due to higher surface roughness, and non-homogeneous surface which contribute to increase probability of chemical reaction between the deposited atoms with the substrate surface. As a result, it decreases the mobility of adatom on the glass B. On the other hand, the lower surface roughness should lead to higher adatom mobility and, as a result, higher (400) orientation in the film structure, as reported by Jung et al. [15].

Larger domain boundary, and smaller grain size of the deposited ITO films may be attributed to higher mobility of adatom on the substrate surface. As discussed by Jung et al. [15], higher adatom mobility leads to higher probability of finding active nucleation sites which, consequently, the coated film represents higher nucleation density on the substrate, smaller grain size, and larger domain boundary. Since the ITO films were deposited simultaneously under the same condition, therefore differences of the domain-grain structure, and the grain size should be attributed to lower surface roughness of the glass A than the glass B. The effect of higher adatom mobility on crystalline structure of the ITO films was also reported by many authors [18-20]. Higher adatom mobility, corresponding to higher energy of adatom on the substrate surface led to more (400) orientation.
Fig. 2 AFM images of ITO coated films at substrate temperature of 450°C on: (a) c-Si wafer, (b) glass A and (c) glass B.

The electrical properties of the ITO films deposited on all substrates are illustrated in Table 2. It can be seen that carrier concentration is $1.63 \times 10^{21}$ cm$^{-3}$ for the ITO films deposited on the c-Si wafer and decreases for that of the glass A, and B which are $9.71 \times 10^{20}$ cm$^{-3}$, and $8.73 \times 10^{20}$ cm$^{-3}$ respectively. It can be noticed that the carrier concentration of the films deposited on each substrate has been relevant to the I(222)/I(400) ratios shown in the Table 1. However, it can be seen that Hall mobilities of all deposited films are not significantly different. It is well known that mechanisms contributing to the carrier concentration are Sn substitution at In sites, and oxygen deficiency in the film structure which have been highly performed during film crystallization, and donate one, and two electrons for charge carriers respectively [11]. However, both mechanisms will result in variations of the lattice parameter from the standard value ($a_0 = 10.118$ Å) of the In$_2$O$_3$ structure. The Sn substitution with a few percent (< 6% at.), and increase of oxygen deficiency in the film structure will lead to decrease of the lattice parameter [8]. On the other hand, higher Sn substitution, and incorporations of Sn and oxygen atoms in the interstitial sites will result in enlargement of the lattice parameter [21]. In addition, it was also reported that deposited ITO film with near-stoichiometric structure donates the (222) preferred orientation, whereas high oxygen deficiency in the film structure results in the (400) preferred orientation [14]. Therefore, from the XRD measurements, as shown in the Fig. 3, higher oxygen deficiency in the film structure should be expected for the ITO film deposited onto the glass A, which, consequently, smaller lattice parameter, and higher carrier concentration compared to the glass B should also be observed. However, from the Table 1, and 2, it can be seen that the lattice parameter for the ITO films on the glass A is remained unchanged, whereas
it becomes smaller than the standard value for the glass B, with small higher carrier concentration for the ITO film on the glass A than that on the glass B. It can be noticed that determined lattice parameter for the glass A contradicts to that reported by many authors [8,14,21], which the lattice parameter decreased with higher oxygen deficiency.

![Fig. 3 XRD spectra of ITO films coated on substrates A, and B at substrate temperature of 450°C.](image)

Observed remained unchanged of the lattice parameter may be due to reduced lattice parameter has been compensated by higher Sn incorporation into the interstitial sites of the bixbyite structure, occurred simultaneously with the former mechanism during film crystallization, which expands the lattice, but, however, it has not contributed to the carrier concentration in the film structure. Therefore, it can be revealed that (i) increase of oxygen deficiency decreases Sn doping efficiency in the film structure, but, on the other hand, it increases migration of Sn atoms into the interstitial site of the bixbyite structure, and (ii) the carrier concentration in the film on the glass A has been contributed mainly from the oxygen deficiency in the film structure. For the glass B, decrease of the lattice parameter can be observed, which may be attributed to a few percent of Sn substitution in the film structure [8], and oxygen deficiency preformed during film deposition. Therefore, it can be concluded that the carrier concentration in the film on the glass B has been contributed from both mechanisms. Optical properties of the bare substrates, and ITO films deposited on both substrates is shown in Fig. 4. The transmittances of the bare substrates A is higher...
than that of the bare glass B, but, however, it shows that transmittances are not different for the ITO coated substrates. The average transmittances are higher than 80% for the ITO films deposited on both substrates. Therefore, it can be concluded that optical properties have not been affected by the surface roughness of the substrates.

Fig. 4 Transmittances of bare and ITO films coated glass A and glass B.

| Substrate types | Average surface roughness (nm) | Crystallite size (222) | Lattice parameter (222) (Å) | I(222)/I(400) |
|-----------------|-------------------------------|------------------------|-----------------------------|---------------|
|                 | Bare substrate | ITO coated films |          |                             |               |
| c-Si wafer      | 0.12             | 0.56             | 20       | 10.109                     | 0.92          |
| glass A         | 0.56             | 0.86             | 27       | 10.118                     | 1.54          |
| glass B         | 2.83             | 1.54             | 37       | 10.091                     | 4.24          |
Table 2 Electrical properties of the ITO films deposited on two kinds of glass substrate at 450°C.

| Substrate types | Carrier concentration (x10²⁰ cm⁻³) | Mobility (cm²/V.s) | Resistivity (x10⁴ Ω.cm) |
|-----------------|-------------------------------------|-------------------|-------------------------|
| c-Si wafer      | 16.3                                | 31                | 1.22                    |
| glass A         | 9.71                                | 31                | 2.12                    |
| glass B         | 8.73                                | 33                | 2.23                    |

4. Conclusions
ITO films deposited by RF magnetron sputtering onto two glass substrates with different surface roughness were analyzed. From the experimental results, it was found that surface morphologies, crystalline structures, and electrical properties of ITO films have been directly affected by the surface roughness of substrates, but it has less influence for their optical properties. Lower surface roughness leads to higher mobility of adatom resulting in larger domain-grain structure, higher (400) orientation, and increase of oxygen deficiency in the film structure. Increase of oxygen deficiency resulted in decrease of Sn doping efficiency the film structure but, on the other hand, increase of Sn incorporation in the interstitial site. The carrier concentration for the ITO film deposited onto the lower roughness substrate has been mainly contributed from the oxygen deficiency rather than the Sn substitution, whereas, it was dominant by the mechanism of Sn substitution for the substrate with higher surface roughness.

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