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Preparation and characterization of nanocrystalline ITO thin films on glass and clay substrates by ion-beam sputter deposition method

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ABSTRACT

Nanocrystalline indium tin oxide (ITO) thin films were prepared on clay-1 (Clay-TPP-LP-SA), clay-2 (Clay-TPP-SA) and glass substrates using ion-beam sputter deposition method. X-ray diffraction (XRD) patterns showed that the as-deposited ITO films on both clay-1 and clay-2 substrates were a mixture of amorphous and polycrystalline. But the as-deposited ITO films on glass substrates were polycrystalline. The surface morphologies of as-deposited ITO/glass has smooth surface; in contrast, ITO/clay-1 has rough surface. The surface roughnesses of ITO thin films on glass and clay-1 substrate were calculated as 4.3 and 83 nm, respectively. From the AFM and SEM analyses, the particle sizes of nanocrystalline ITO for a film thickness of 712 nm were calculated as 19.5 and 20 nm, respectively. Optical study showed that the optical transmittance of ITO/clay-2 was higher than that of ITO/clay-1. The sheet resistances of as-deposited ITO/clay-1 and ITO/clay-2 were calculated as 76.0 and 63.0 Ω/□, respectively. The figure of merit value for as-deposited ITO/clay-2 ($12.70 \times 10^{-3}/\Omega$) was also higher than that of ITO/clay-1 ($9.6 \times 10^{-3}/\Omega$), respectively. The flexibilities of ITO/clay-1 and ITO/clay-2 were evaluated as 13 and 12 mm, respectively. However, the ITO-coated clay-2 substrate showed much better optical and electrical properties as well as flexibility as compared to clay-1.

1. Introduction

Indium tin oxide (ITO) thin film is a wide band gap semiconductor with good conductivity and high optical transmission within the visible spectrum [1]. ITO thin films are used in a wide variety of applications, including solar cell and other optoelectronic devices; ITO film is suitable for a window layer or a transparent back contact. Recently the research and development have been concentrating on preparation and characterization of flexible dye sensitized solar cell. Glass substrates can be used for solar cell application, but glass is very brittle, and is too heavy, especially for large-area solar cell devices. These disadvantages can be overcome by using flexible substrates, which are light-weight and inexpensiveness. Optically transparent plastics with high glass transition temperatures are desired for many optoelectronic devices. In addition, they need to withstand the growth conditions of metal oxides while maintaining their mechanical and optical properties. If we want to apply the ITO coated flexible substrates for flexible dye sensitized solar cell applications, the thermal resistant stability of flexible substrates should be maximum (~450 °C). Because the amorphous phase of TiO_2 can be changed into anatase phase after the heat treatment in the range of 400–500 °C.

The preparation and characterization of stress free ITO film on flexible substrate with high electrical conductivity and optical transmittance are very important for device applications [2]. In order to prepare the stress free film, the lattice and thermal match between substrate and film are also important. The thermal expansion coefficients of In_2O_3, polyethylene terephthalate (PET), glass, and polycarbonate (PC) were reported as 7.2×10^{-6}, 12×10^{-6}, 4.6×10^{-6} and 39×10^{-6}/°C, respectively. The deformation temperatures of PET and PC were reported as 220 and 140 °C, respectively [3,4]. Therefore, the plastic substrates cannot be applied for the crystallization of amorphous TiO_2 in the temperature range of 400–500 °C. Recently Tetsuka et al. [5] fabricated the flexible transparent clay substrate; it has more flexibility and high thermal resistance. The clay substrates can withstand heat up to 460 °C and the thermal expansion coefficient of the clay (3×10^{-6}/°C) coincides well with the glass thermal expansion coefficient. Particularly the lattice constant of ITO is well matched with that of clay substrate (the lattice match substrate is very suitable for device fabrication).

In this work, we have used the ion-beam sputter deposition (IBSD) method to prepare nanocrystalline ITO thin films, because the ITO film grown by IBSD can be crystallized at low temperature. Generally it was reported that the crystallization temperature of ITO is in the range of 100–250 °C [6]; but in the present work, the as-deposited ITO films by IBSD are polycrystalline. So IBSD is a more suitable method compared to r. f. reactive sputtering, pulsed laser

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deposition, electron beam evaporation etc. In the present work, we study the effect of substrate surface roughness on the surface morphological, structural, optical and electrical properties of ITO films grown on flexible transparent clay substrates with high heat resistance over 450 °C. In order to check the effect of substrate surface roughness on the surface morphological, structural, optical and electrical properties of ITO films, the ITO thin films were also deposited on glass substrates.

2. Experimental details

ITO thin films were deposited on glass and flexible clay [Clay-TPP-LP-SA (40 μm thick) and Clay-TPP-SA (48 μm thick)] substrates using ion-beam sputter method at room temperature. The preparation method of clay substrate is found elsewhere [5,7,8]. The composition of the target was 90 wt.% In_2O_3 and 10 wt.% SnO_2, with a purity of 99.99%. Prior to deposition, the system was evacuated to a base pressure of 1×10^{-4} Pa by turbo-molecular pump and then back filled with high purity argon (Ar) and oxygen (O_2 = 3%) gases. The flow rate was controlled by mass flow controller. The acceleration voltage for sputtering was fixed at 2500 V. Some ITO samples were annealed under a vacuum of -90 mPa at 250 °C. In the present work, ITO thin films were grown under fixed preparation conditions. The thickness of the ITO film was measured by stylus profilometer (Surfcorder, ET 4000M, Kosaka Laboratory Ltd.). The surface morphologies of the ITO films were observed by field emission scanning electron microscopy (FESEM, S4800, Hitachi). The surface roughness of ITO thin films was studied by atomic force microscopy (AFM, Nanoscope IIIa, Veeco Instruments) in tapping mode. The structural properties of the ITO films were analyzed by X-ray diffraction (XRD) [RINT 2200VK/PC, Rigaku; λ = 1.54056 Å; X-ray 40 kV/30 mA]. The optical transmittance spectra of ITO films on clay and glass substrates were measured using an UV-Vis-NIR spectrophotometer (UV-3150, Shimadzu) in the wavelength range from 280 to 2200 nm; uncoated clay and glass substrates were used as reference. The sheet resistance of the ITO films was measured by digital multimeter.

3. Results and discussion

3.1. Structural properties

ITO thin films were deposited on glass, clay-1 [Clay-TPP-LP-SA] and clay-2 [Clay-TPP-SA] substrates under a fixed deposition conditions. The ITO film thickness was measured as 422 ± 10 nm. Fig. 1 shows the X-ray diffraction patterns of as-deposited ITO thin films on clay-1, clay-2 and glass substrates. XRD patterns show that the ITO films on clay-1 and clay-2 substrates are a mixture of amorphous and polycrystalline (see Fig. 1a and c), and the diffraction peak observed at 28.70° corresponds to clay substrate. On the other hand, the as-deposited ITO films on glass substrate are polycrystalline and it has a strong preferred orientation along (4 0 0) direction of cubic In_2O_3 (see Fig. 1b). XRD result shows that the as-deposited ITO films on clay-1 and clay-2 substrates exhibit poor crystallinity, but ITO film deposited on glass substrate at room temperature exhibits good crystallinity. That is, the crystallinity of ITO films on glass substrate is better than that on clay-1 and clay-2 substrates. It shows that the bombarding ions are energetic enough for the crystallization of ITO on glass substrate than that on clay-1 substrate. It is attributed that the crystallization temperature of ITO layer can be easily attained on glass substrate during deposition [9]. The lattice parameter of as-deposited ITO on glass is calculated as 10.360 Å.

The as-deposited ITO films change from amorphous into polycrystalline as the film thickness is increased from 422 ± 10 nm to 712 ± 10 nm. Fig. 1d and e show the XRD patterns of as-deposited ITO film on glass and clay-1 substrates for a film thickness of 712 ± 10 nm. The ITO film deposited on clay-1 substrate has shown the preferred orientation along (2 2 2) direction. In contrast, the orientation of ITO film on glass substrate is in (4 0 0) direction. The ITO film on clay-1 substrate shows an intense (2 2 2) plane. This preferential orientation of the ITO film arises from the excellent lattice match between ITO film and saponite [10]. The FWHM value for ITO/clay-1 is larger than that of ITO/glass (see Table 1). It reveals that ITO films deposited on glass substrate have much better crystallinity than those on clay-1 substrate. The lattice parameters are calculated as 10.383 and 10.123 Å for ITO/glass and ITO/clay-1, respectively. The lattice parameter of bulk In_2O_3 was reported as 10.118 Å. The increase in lattice parameter is attributed to the incorporation of Sn ions in the interstitial positions or substitutional incorporation of Sn^{2+} ions into In^{3+} ions. The lattice parameter of bulk In_2O_3 doped with 10% SnO_2 was reported as 10.136 Å [11]. It shows that the increase in lattice parameter for 10% SnO_2 doped In_2O_3 is only 0.18%. The stress in the films is one of the main reasons for the large variation in lattice parameter of ITO films and the magnitude of stress in the as-deposited films is strongly related to the microstructure of the films [12]. It may also be related to the oxygen deficiency and strain due to the difference in thermal expansion coefficient between the ITO film (8.5×10^{-6}/°C) and glass substrate (4.6×10^{-6}/°C) and clay-1 substrate (3×10^{-6}/°C). But in the present work, the thermal stress between the film and substrates is found to be negligible; because the thermal stress in the room temperature deposited ITO films is zero [13]. The internal stress in the film can be calculated from the following relation

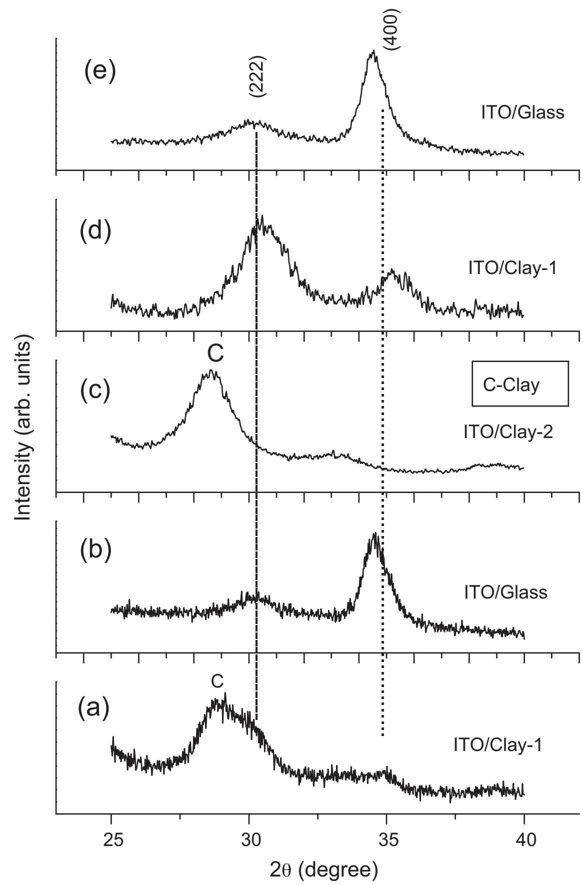

Fig. 1. X-ray diffraction patterns of as-prepared ITO thin films: (a–c) ITO thin films on clay-1, glass and clay-2 substrates, respectively, for a film thickness of 422 ± 10 nm; (d and e) ITO thin films on clay-1 and glass substrates, respectively, for a film thickness of 712 ± 10 nm.