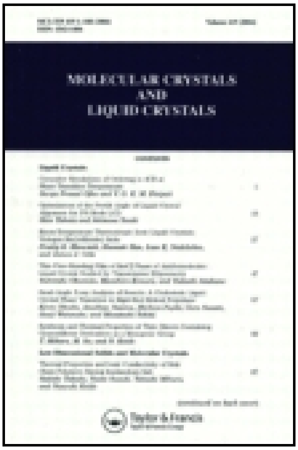

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FABRICATION OF WELL-ORDERED INDIUM-TIN-OXIDE FILM AND CHARACTERIZATION OF ORGANIC FILMS VACUUM-DEPOSITED ON IT

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FABRICATION OF WELL-ORDERED INDIUM-TIN-OXIDE FILM AND CHARACTERIZATION OF ORGANIC FILMS VACUUM-DEPOSITED ON IT

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Indium-tin-oxide film (ITO) was fabricated on a (100) surface of an yttria-stabilized zirconia (YSZ) single crystal by pulsed laser deposition. The ITO film was characterized by atomic force microscopy and X-ray diffraction measurements. ITO grew heteroepitaxially on the YSZ substrate. The ITO film surface was extremely flat and roughness in height was less than 1 nm. Two organic dyes, copper phthalocyanine and vanadyltetraphenylporphyrin, were vacuum-deposited on the ITO substrate. Their molecular orientations in thin film were investigated by transmission electron microscopy and electron diffraction analysis.

Keywords: heteroepitaxy; indium-tin-oxide (ITO); organic dyes; vacuum-deposition

1. INTRODUCTION

Recently, organic thin films have been received considerable interest. In fact, they have been found various applications such as organic light-emitting-diodes, photovoltaic devices and thin film transistor. Since these organic devices have layered structure, optical and electrical properties depend greatly on their crystal structures and the interface. For example, Nakayama *et al.* have reported the photocurrent multiplication at organic/metal interface [1]. Nowadays, it is very important to control the interfacial

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structure between electrodes and organic layers. However, there were few reports on control of interfacial structure between organic layer and electrode [2,3], because electrodes used as a substrate are composed of polycrystalline films and have rough surface. Especially, indium-tin-oxide (ITO) film, which is most widely used as a transparent electrode, is almost polycrystalline. Thus further investigation of organic/ITO interface is very difficult. To investigate interfacial structure, well-ordered and smooth ITO film is strongly required.

Adurodija *et al.* have reported that an ITO film deposited on a glass plate by pulsed laser deposition (PLD) oriented in the [111] direction [4,5]. However, each crystal size of grain was small (200–400 nm). Recently, the well-ordered ITO thin film was prepared on an yttria-stabilized zirconia (YSZ) single crystal substrate [6,7]. The grain size depends on the substrate temperature. In this study, ITO film was prepared on a YSZ single crystal (ITO/YSZ film) by PLD and organic dyes were vacuum-deposited on it. The morphology and orientation of the ITO/YSZ film and the structure of organic thin films are investigated.

2. EXPERIMENTAL

An ITO film was deposited in a vacuum chamber with a KrF ($\lambda = 248$ nm) eximer laser (Lambda Physik, COMPex 102) system. The laser system was operated at total energy of approximately 230 mJ and a pulse frequency of 5 Hz. The laser beam was concentrated on a target using a spherical lens with a focal length of 250 mm, thus producing an energy density of approximately 3 J/cm^2. Commercially available high purity (99.997%) Sn-doped In_2O_3 (5 wt%) sintered ceramics (Japan Energy Company) with a packing density of 98% was used as a target. The ITO was deposited on a (100) surface of a YSZ single crystal (Earth Chemical Co., Ltd). Background pressure of the deposition chamber was 5×10^{-4} Pa, and the oxygen pressure was kept at 1.3 Pa during deposition. The substrate was kept at 800°C. The morphology and structure of ITO film were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) measurements. XRD measurements were performed 2θ-fixed θ scans (out-of-plane rocking curve) and $2\theta_\chi$-fixed ϕ scans (in-plane rocking curve). The resistivity, Hall mobility, and carrier density of the ITO film were determined by van der Pauw measurement.

The chemical formulae of two organic dyes used here, copper phthalocyanine (CuPc) and vanadyltetraphenylporphyrin (VOTPP), are shown in Figure 1. These samples were purified by vacuum sublimation prior to deposition. They were vacuum-deposited on a commercially available ITO glass substrate (NIPPON SHEET GLASS Co., Ltd.) and the ITO/YSZ

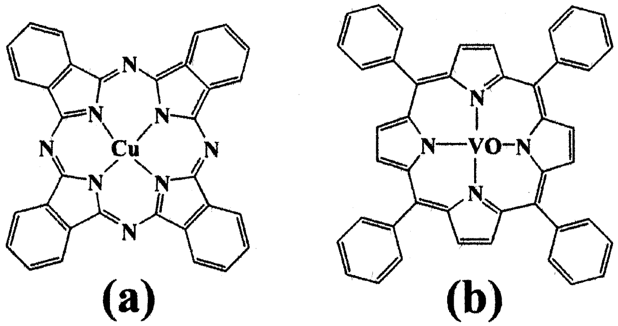

FIGURE 1 Molecular structures of CuPc (a) and VOTPP (b).

substrate kept at 150°C under the pressure at 1.0×10^{-3} Pa. The deposition rate was controlled to be about 0.5–1 nm/min in thickness. The thickness of organic films was controlled to be about 30 nm. The structure of organic thin films was characterized by transmission electron microscopy (TEM) and electron diffraction (ED) analysis.

3. RESULTS AND DISCUSSION

3.1. ITO Films

Figures 2(a) and (b) show typical AFM images of the commercially available ITO glass (ITO/glass film) and the ITO/YSZ substrate. The former was fabricated on the glass plate by sputtering. The ITO/glass film was composed of granules with 300–500 nm in diameter contained small sub

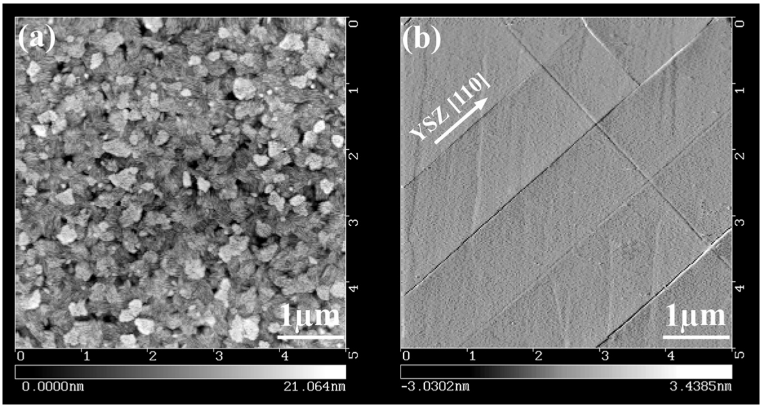

FIGURE 2 AFM images of the ITO/glass film (a) and the ITO/YSZ film (b).

boundary structure [8]. On the other hand, the ITO/YSZ film showed quite different surface morphology in comparison with the ITO/glass film. Cracks were observed along the [110] direction of the YSZ crystal used as a substrate. These cracks may originate from the difference in the thermal expansion coefficients between the YSZ substrate and the deposited ITO film [6]. The height profile revealed that the surface of the ITO/YSZ film was extremely flat. The roughness was less than 1 nm, except for cracks.

Figures 3(a) and (b) show θ–2θ XRD patterns of the ITO/glass film and the ITO/YSZ film, respectively. The ITO/glass film showed a lot of diffraction peaks. This means that the film had no prior orientation and was polycrystalline. On the other hand, the ITO/YSZ film showed only intense peaks of ITO (h00) and YSZ (h00). This finding indicates that the ITO film took preferential [100] orientation on the YSZ substrate. On the other hand, θ–$2\theta_\chi$ XRD pattern of the ITO/YSZ film showed only intense peak around 34.8°, as shown in Figure 4. It is noted that the peak was broadening at the higher angle region. The peak was separated to two peaks, YSZ (200) and ITO (400). The ITO film deposited on the YSZ substrate grew heteroepitaxially with the orientation relationship of $[010](h00)_{ITO}$// $[010](h00)_{YSZ}$. However, ITO (400) peak was shift to the higher angle in

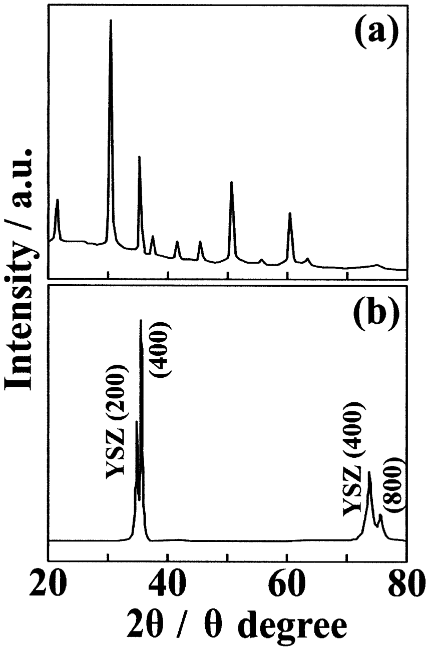

FIGURE 3 XRD (θ–2θ) patterns of the ITO/glass film (a) and the ITO/YSZ film (b).

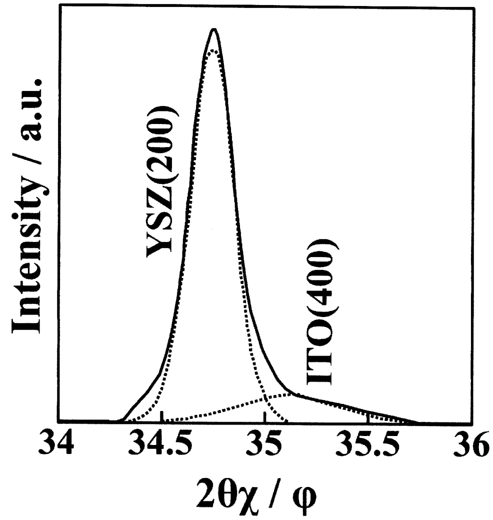

FIGURE 4 XRD (ϕ–$2\theta_\chi$) pattern of the ITO/YSZ film.

comparison to the diffraction angle in the measurement of θ–2θ scans. Izumi *et al.* have already observed such peak shift [9]. The lattice misfit between YSZ (cubic structure, lattice constant $2a_{YSZ} = 1.028\,\text{nm}$) and ITO (cubic bixbyite structure, $a_{ITO} = 1.012\,\text{nm}$) is 1.6%. The peak shift may originate from the misfit that causes in-plane residual stress.

The resistivities of commercially available ITO are $1–3 \times 10^{-4}\ \Omega\text{cm}$. On the other hand, the resistivity, Hall mobility and carrier density of the ITO/YSZ film were $2.2 \times 10^{-4}\ \Omega\text{cm}$, $24\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $1.2 \times 10^{21}\,\text{cm}^{-3}$, respectively. The electrical properties of epitaxially grown ITO film are the same to that of commercially available ITO film. It seems that crystal size and orientation are not dominant to electrical properties of ITO film.

3.2. Organic Thin Films Deposited on ITO Films

Figures 5(a) and (b) show TEM images of CuPc film deposited on the ITO/glass and the ITO/YSZ substrates. CuPc film deposited on the ITO/glass substrate was composed of fiber-like crystals. The length of these crystals was less than 1 μm. CuPc film deposited on the ITO/YSZ substrate showed also similar morphology to that on ITO/glass substrate. However, CuPc crystals grew larger (5–10 μm), which originates from the flatness of the ITO surface. It is well known that the growth of vacuum-deposited film takes place in a combination process of adsorption, migration and rearrangement of the evaporant molecules on the substrate. Adsorbed site of the evaporant molecule is heavily dependent on the surface morphology of

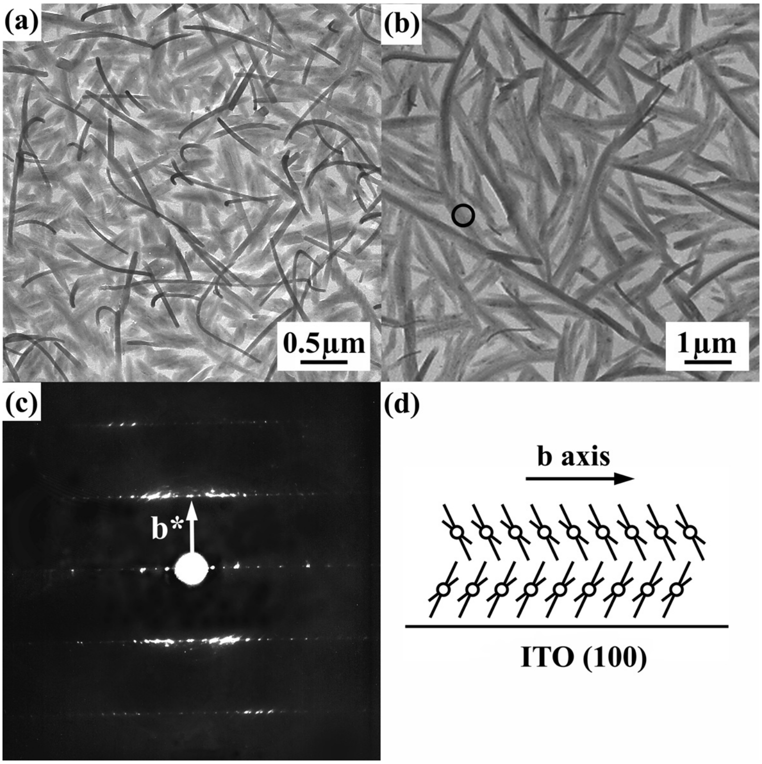

FIGURE 5 TEM images of CuPc films deposited on the ITO/glass substrate (a) and on the ITO/YSZ substrate (b). ED pattern (c) from selected area indicated by a circle in (b). A schematic diagram of molecular orientation in CuPc film (d).

the substrate because the surface energy at the grain boundary and/or the step is higher than that of smooth surface. Nucleation of crystal growth occurs at higher surface energy region. The more the number of the grain boundary increases, the more the number of the nuclei. There are many grain boundaries in the ITO/glass substrate. Therefore, CuPc on the ITO/glass substrate forms small crystals. Figure 6(c) shows ED pattern from the selected area indicated by a circle in Figure 5(b). The ED pattern showed a fiber pattern whose fiber period was 0.38 nm. The crystal structure of CuPc has isomorphic and they have at least two polymorphs, a metastable α-form (monoclinic, $a = 2.592$ nm, $b = 0.379$ nm and $c = 2.392$ nm, $\beta = 90.4°$) and a stable β-form (monoclinic, $a = 1.941$ nm, $b = 0.479$ nm and $c = 1.463$ nm, $\beta = 120.56°$). On comparison of the observed interplanar spacings and the calculated ones, it was found that CuPc crystallized in α-form. The fiber period of 0.38 nm corresponds to the

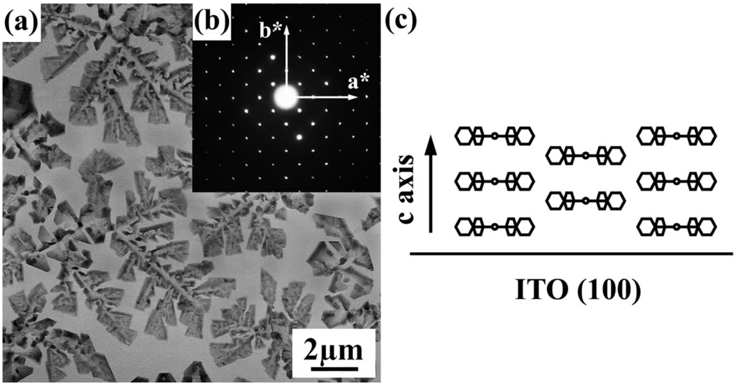

FIGURE 6 TEM image (a) and ED pattern (b) of the VOTPP film deposited on the ITO/YSZ substrate, and a schematic diagram of molecular orientation in VOTPP film (c).

periodic distance of (010) plane of CuPc crystal. This finding indicates that the b-axis of CuPc crystal aligned parallel to the ITO surface and molecular planes were adsorbed obliquely to the substrate surface, as shown in Figure 5(d).

VOTPP film deposited on the ITO/glass substrate was composed of randomly oriented trapezoid and granular crystals. On the other hand, VOTPP deposited on the ITO/YSZ substrate formed only trapezoid crystals. Figure 6 shows TEM image (a) and ED pattern (b) of VOTPP film deposited on the ITO/YSZ substrate. The ED pattern showed single net pattern with the diffraction spots corresponding to the interplanar spacing of 0.94 nm. VOTPP crystal belongs to tetragonal and crystal parameters are $a = 1.3345$ nm and $c = 0.9745$ nm. The ED pattern of Figure 6(b) coincided with the net pattern projected along the c axis of the VOTPP crystal. From the mutual relationship between the substrate crystal and the deposited crystal, it is concluded that molecular planes of VOTPP oriented parallel to the substrate surface, as shown in Figure 6(c).

CONCLUSION

ITO grew heteroepitaxially on a (100) surface of the YSZ single crystal. The surface of the ITO/YSZ substrate was extremely flat. CuPc and VOTPP crystals grew larger on the ITO/YSZ substrate than on the ITO/glass substrate. The crystal size depended on the flatness of the ITO substrate. The ED pattern of CuPc film deposited on the ITO/YSZ substrate indicated that the molecular planes of CuPc were adsorbed obliquely to the substrate surface. On the other hand, VOTPP molecules on the ITO/YSZ substrate were adsorbed parallel to the substrate surface.

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