Controlling plasmonic properties of epitaxial thin films of indium tin oxide in the near-infrared region

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Abstract. Epitaxial thin films of indium tin oxide (ITO) were grown on yttria-stabilized zirconia single-crystal substrates by using a pulsed laser deposition to examine their plasmonic properties. The dielectric function of ITO was characterized by spectroscopic ellipsometry. Through the concentration of SnO$_2$ in the target, the carrier concentration in the films was modified, which directly leads to the tuning of the dielectric function in the near-infrared region. Variable-angle reflectance spectroscopy in the Kretschmann geometry shows the dip in the reflection spectrum of $p$-polarized light corresponding to the excitation of surface plasmon polaritons (SPPs) in the near-infrared region. The excitation wavelength of the SPPs was shifted with changing the dielectric functions of ITO, which is reproduced by the calculation using transfer matrix method.

1. Introduction
Surface plasmon polaritons (SPPs) are the collective oscillations of conduction electrons coupled to the electromagnetic waves propagating at the interface between a metal and a dielectric. The electric field of SPPs is evanescently confined at the interface and accumulated in the scale below the diffraction limit of light [1]. These properties of SPPs have attracted attention in various fields [2, 3].

Noble metals, especially silver and gold, are almost exclusively used as conventional plasmonic materials. Their plasma frequency ($\omega_p$) is suitable for SPPs applications in the visible region. In contrast, they do not work effectively as a plasmonic material in the infrared region [4]. Since the infrared region is technically important in the field such as telecommunication and sensing, complementary plasmonic materials are required that operate in this region [5]. Transparent conductive oxides, such as indium tin oxide (ITO) and gallium-doped zinc oxide (GZO), have been explored as alternative plasmonic materials because of their variable $\omega_p$ and their small optical losses in the infrared region [4-8].

ITO has been fabricated by various techniques such as sputtering and pulsed laser deposition (PLD) [6-9]. The lowest resistivity has been achieved for epitaxial thin films on yttria-stabilized zirconia (YSZ) substrates by using PLD technique [9]. Because the lattice constant of ITO matches well twice of the lattice constant of YSZ [7, 9], ITO grows epitaxially and shows high crystallinity with a low concentration of defects to minimize a scattering of electrons.

In the present study, we have fabricated epitaxial ITO thin films on YSZ substrates by PLD technique, and controlled the dielectric function by changing the concentration of SnO$_2$ in the target. The dielectric function in the near-infrared region was obtained from spectroscopic ellipsometry (SE). By increasing the SnO$_2$ concentration in the target, we have obtained thin film showing the highest $\omega_p$ among the ITO films for SPPs applications.
2. Experiment
Commercially available YSZ (111) single crystal substrate was annealed at 1350 °C in air to obtain atomically flat surface. In$_2$O$_3$ mixed with 10 and 20 wt% SnO$_2$ was pelletized and sintered at 1400 °C in air and used as a target. The deposition was done at the oxygen pressure of $1.2\times10^{-3}$ Pa, and the substrate temperature of 600 °C. A KrF excimer laser ($\lambda = 248$ nm, repetition rate = 5 Hz, pulse energy = 4 J cm$^{-2}$ pulse$^{-1}$) was used to ablate the target. Two thin films with different SnO$_2$ concentrations have been prepared from the target with 10 and 20 wt% SnO$_2$, which are hereafter labelled as ITO–10 and ITO–20, respectively.

Crystallinity and orientation of ITO thin films were analyzed by x-ray diffraction (XRD) (ATX-G, Rigaku Co.). The thickness and the dielectric function of the thin films were measured by SE (M2000, J. A. Woollam Japan). The excitation of SPPs on the thin films was examined by variable-angle reflectance spectroscopy under the Kretschmann geometry [1].

3. Results and discussion
3.1. Structural characterization
Figures 1(a) and (b) show the out-of-plane XRD patterns of ITO–10 and ITO–20 grown on YSZ (111) substrates, respectively. The intense peaks of the ITO 222 and 444 are observed, along with the peaks of YSZ 111 and 222. In-plane XRD measurements (not shown here) confirm the intense peak of ITO 440 along with the peak of YSZ 220; other diffraction peaks were not observed. In-plane and out-of-plane XRD patterns demonstrate that the thin films were grown heteroepitaxially on YSZ substrates. The insets of Figures 1(a) and (b) show the rocking curve of the peak of ITO 222, and the full width at half maximum (FWHM) of ITO–10 and ITO–20 are 0.031° and 0.039°, respectively. These values are on the same order of the smallest value for atomically-flat ITO thin film (0.015°) [9]. The FWHM is larger for ITO–20, indicating the decrease of the crystallinity with increasing Sn concentration.

![Figure 1. Out-of-plane XRD patterns of ITO–10 (a) and ITO–20 (b). The inset shows the out-of-plane rocking curve of the peak of ITO 222.](image)

3.2. Optical properties
In analysis of the SE data, we employed a function with a Drude term and a Gaussian term to describe the dielectric function of the ITO. The Drude term and Gaussian term denote the contribution from the collective oscillation of free electrons and the interband transition of bound electrons, respectively [10]. The Drude term is given as follows:

$$\varepsilon_{\text{Drude}} = \frac{\omega_p^2}{\omega^2 + \gamma_p^2} - \frac{\gamma_p}{\omega (\omega^2 + \gamma_p^2)} \frac{i}{\varepsilon_0 m^* \mu} \left(1 - \frac{\omega_p^2}{\omega^2} \right)$$

(1)

where $\omega$ is the frequency. Plasma frequency $\omega_p$ and damping factor $\gamma_p$ are described as a function of carrier concentration $n$ and mobility $\mu$, respectively, as $\omega_p = \sqrt{\frac{n q^2 (enm^*)}{\varepsilon_0}}$ $\omega_p^2$ and $\gamma_p = \frac{q}{m^* \mu}$, with $\varepsilon_0$ the permittivity of free space, $q$ and $m^*$ the charge and the effective mass of electron.
Figure 2 shows the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric functions of ITO–10 and ITO–20 calculated from the SE data. Also plotted are the dielectric functions of the ITO thin films reported in refs. 6 and 8. The crossover wavelength, where the $\varepsilon'$ crosses zero, of ITO–10 and ITO–20 are 1290 and 1140 nm, respectively. The value for ITO–20 is the shortest among the ITO thin films prepared for plasmonic purpose to date. Figure 2(b) shows that the $\varepsilon''$ of ITO–10 is the smallest in the range of the plot.

![Figure 2. Real (a) and imaginary (b) parts of the dielectric functions of ITO–10 and ITO–20. Dielectric functions of ITO thin films reported in literatures are also plotted [6, 8].](image)

Table 1 summarizes the $n$ and $\mu$ for ITO–10 and ITO–20 evaluated from the Drude term of the fitting function, together with those in refs. 6 and 8. ITO–20 has the largest $n$, reflecting its shortest crossover wavelength, while ITO–10 shows the largest $\mu$, which is in accordance with the lowest $\varepsilon''$. Also the high mobility for ITO–10 and ITO–20 agrees well with the crystallinity evaluated by XRD measurements.

**Table 1.** The carrier concentration ($n$) and mobility ($\mu$) for ITO–10 and ITO–20 obtained from SE data. The values reported in the literatures [6, 8] are also tabulated.

|        | $n$ (cm$^{-3}$) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) |
|--------|----------------|--------------------------------|
| ITO–10 | $0.98 \times 10^{21}$ | 47.6 |
| ITO–20 | $1.23 \times 10^{21}$ | 40.6 |
| Losego et al. [6] | $1.2 \times 10^{21}$ | 35 |
| Noginov et al. [8] | $1.17 \times 10^{21}$ | 43.2 |

3.3. Plasmonic properties

Figures 3(a) and (b) show the reflectance ratio as a function of incident angle and wavelength for ITO–10 and ITO–20, respectively, with the inset illustrating the schematic setup of the experiment. The $p$-polarized reflectance $R_p$ is divided by $s$-polarized reflectance $R_s$ because the SPPs are excited only by $p$-polarized waves. In Fig. 3(a), the dip in reflectance ratio, caused by the excitation of SPPs at the interface between the ITO–10 and air, is observed at $48^\circ$ and around 1600 nm. In Fig. 3(b), that is, in the case of ITO–20, the dip is blue-shifted to 1400 nm.

The reflectance spectra of the samples were calculated by using transfer matrix method [11], as shown in Figs. 3(c) and (d). The inset illustrates the model for the calculation. The model consists of prism, substrate, ITO–10 or ITO–20, and air. The thickness ($t$) and the refractive index ($n$) of the layers were set as follows; prism ($t$ = infinite, $n$ = 1.78), YSZ substrate ($t$ = 0.5 mm, $n$ = 2.1), ITO–10 ($t$ = 230 nm, $n$ from Fig. 2), ITO–20 ($t$ = 125 nm, $n$ from Fig. 2), and air ($t$ = infinite, $n$ = 1). Comparing the experimental results with the calculations, it is found that the reduction of reflectance caused by the excitation of SPPs is observed at the similar wavelength region. The experimental data and the calculation agree well with each other.
Figure 3. Reflectance spectra of ITO–10 (a) and ITO–20 (b) as a function of incident angle and wavelength. The inset shows the sample setup. Calculated reflectance spectra of ITO–10 (c) and ITO–20 (d) by using transfer matrix method. The inset shows the model for calculation.

4. Conclusion
We have experimentally demonstrated the tuning of SPPs wavelength in ITO thin film through $n$ and $\mu$. ITO thin films were epitaxially grown on YSZ substrates by PLD technique, and the dielectric functions in the range of 800-1700 nm were evaluated by SE measurement. The variable-angle reflectance spectroscopy shows the excitation of SPPs at the angle and the wavelength predicted from the dielectric functions of the thin films. The crossover wavelength for ITO–20 is shorter than those of ITO thin films reported so far.

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