Preparation of Nb-doped Anatase Type TiO$_2$ Epitaxial Thin Films and Excitation of Surface Plasmon Polaritons

Shunsuke MURA$^{1,2*}$, Ryosuke KAMAKURA$^1$, Koji FUJITA$^1$, Yohei DAIKO$^1$ and Katsuhisa TANAKA$^1$

$^1$Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.
$^2$PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan.

Received September 19, 2016; Revised November 8, 2016; Accepted November 24 2016

ABSTRACT

We have fabricated highly crystallized thin films of niobium-doped anatase type titania (Ti$_{1-x}$Nb$_x$O$_2$) to examine the relationship between the electronic transport properties and the plasmonic response. Ti$_{1-x}$Nb$_x$O$_2$ thin films were epitaxially grown on LaTiO$_3$ substrates by using pulsed laser deposition. Attenuated total reflectance spectra in the infrared (IR) region measured using the Otto configuration show a dip for p-polarized light, corresponding to an excitation of surface plasmon polaritons. The IR reflectivity data can be well reproduced by the theoretical calculation based on the Fresnel model, in which the dielectric function of Ti$_{1-x}$Nb$_x$O$_2$ can be modeled by the combination of a Lorentz term and a Drude term. The real part of dielectric function for Ti$_{1-x}$Nb$_x$O$_2$ ($x = 0.03$) is negative at the wavelengths longer than 2.78 μm in the IR region.

KEY WORDS

Nb-doped anatase type TiO$_2$, surface plasmon polariton, transparent conductive oxide

1 Introduction

Surface plasmon polariton (SPP) is a coupled wave of the plasma oscillation of electrons and the electromagnetic wave and propagates at an interface between a metal and a dielectric ($^1$). SPP achieves confinement of electromagnetic oscillations with optical frequency to nanoscale dimensions and enhances local electromagnetic fields, leading to a wide range of applications.

Transparent conductive oxides, such as indium tin oxide (ITO), and F-doped SnO$_2$ (FTO) have the carrier density on an order of $10^{20}$ to $10^{21}$ cm$^{-3}$ and show the plasma frequency in the infrared (IR) region ($^2$-$^2$). Thus they can support SPP in the IR region. In addition, there have been emerging compounds based on earth abundant elements as sustainable alternatives to the ITO. Aluminum- or gallium-doped ZnO has been shown to be a suitable low-cost and highly available substitute for ITO in some applications ($^3$-$^5$). Recently, Nb-doped anatase type TiO$_2$ (Ti$_{1-x}$Nb$_x$O$_2$) with its low cost, nontoxicity, earth abundance, and both thermal and chemical stability has received attention ($^6$-$^{10}$). It has been shown that anatase Ti$_{1-x}$Nb$_x$O$_2$ can exhibit an electronic conductivity comparable to that of ITO while maintaining high optical transparency in both visible and IR regions. Ti$_{1-x}$Nb$_x$O$_2$ also possesses a high refractive index that is of particular interest for use as transparent electrodes for solar cells and GaN-based LEDs ($^11$-$^{13}$). So far, Ti$_{1-x}$Nb$_x$O$_2$ has been obtained in the form of films via vapor phase depositions ($^{14,16,18-24}$) and sol–gel ($^{26-31}$), and also in the form of nanocrystals ($^{32-39}$). While Ti$_{1-x}$Nb$_x$O$_2$ has been actively studied in a context of transparent electrodes, exploration of its plasmonic properties is limited ($^{40}$). The experimental studies on the thin films of Nb:TiO$_2$ so far examined the plasmonic properties only indirectly via optical transmission, Fourier transform IR (FT-IR) and ellipsometry measurements: Although these measurements can detect the presence of conducting electrons which causes the increase in reflectance, they cannot excite the SPPs directly because of the momentum mismatch between the SPP and the light.

In the present study, we have prepared an epitaxial thin film of anatase-type Ti$_{1-x}$Nb$_x$O$_2$ and excited SPPs on the surface by using an attenuated total reflectance geometry to match the momentum. The carrier density ($n$) and mobility ($\mu$) are calculated from Hall effect measurement, and are confirmed to be consistent with the values estimated from the optical measurements. The dielectric function deduced from the data of FT-IR measurement shows that the thin film is metallic for the wavelength longer than 2.78 μm.

2 Experimental

We fabricated anatase type Ti$_{1-x}$Nb$_x$O$_2$ thin films on synthetic LaTiO$_3$ (LAO) (100) single-crystal substrates by using a pulsed laser deposition with a KrF excimer laser. Rutile type Ti$_{1-x}$Nb$_x$O$_2$ ceramics ($x = 0, 0.03$) with high density were utilized as the PLD target. The
chamber pressure of O₂ was 1.3 × 10⁻¹ Pa, and the substrate was heated to 660°C during the deposition. Identification of crystalline phase and orientation was analyzed by x-ray diffraction (XRD). A Hall effect measurement was performed by using a standard four point probe at room temperature to obtain n, μ, and resistivity of the sample.

The excitation of SPP on the thin film was examined by attenuated total reflectance spectroscopy using a FT-IR spectrometer (Nicolet6700, Thermo Fisher) with a variable angle reflectance equipment (Seagull, Harrick). The sample was placed in contact with a prism (zinc selenide) and a four layer system with an air, a film, and a substrate as shown in Fig. 2 (c), which corresponds to the Otto configuration. When x = 0, a dip appears at a low frequency region (wavenumber = 650 cm⁻¹), which is a phonon mode of the thin film. No other dips appear in the spectra. There is additional dip in reflectance when x = 0.03 at about the wavenumber of 1320 cm⁻¹, corresponding to the wavelength of 7.58 μm. This dip is caused by the excitation of SPP at the interface between the Ti_{1−x}NbO₂ and the air. The wavenumber of the dip increases as the angle of incidence increases, following the dispersion of SPP.

The features of reflectance spectra are accurately described by a four phase Fresnel model. Here, the total reflectivity (r) of the four-layer system is given by,

\[ r = \frac{r_{12} + r_{23} \exp(i2k_d d_2)}{1 + r_{23} \exp(i2k_d d_2)} \tag{1a} \]

with

<table>
<thead>
<tr>
<th>x</th>
<th>n (cm⁻¹)</th>
<th>μ (cm² V⁻¹ s⁻¹)</th>
<th>conductivity (Ω⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>8.3 × 10²³</td>
<td>9.6</td>
<td>1.27 × 10⁵</td>
</tr>
</tbody>
</table>

Table 1  Transport properties of Tiₙ₋₁NbₙO₂ thin film (x = 0.03) obtained by Hall effect measurement.
described as a function of \( \varepsilon_2 \) was a variable parameter. Note that permittivity. Plasma frequency \( p \) and damping factor \( \gamma \) affect the thickness of the medium \((i = 1, 2, 3, \text{and } 4)\). The thickness of the Ti

\[ r_{34} = \frac{r_{34} \exp(2k_i d_i)}{1 + r_{2}r_{4} \exp(2k_i d_i)}, \quad (1b) \]

\[ k_e = \frac{\omega}{c}[\varepsilon_0 - \varepsilon_0 \sin(\theta_1)]^{1/2}, \quad (1c) \]

and

\[ r_{\varphi} = \frac{k_e - k_p}{k_e + k_p}, \quad (1d) \]

for s-polarized light and

\[ r_{m} = \frac{\varepsilon_r k_e - \varepsilon_r k_p}{\varepsilon_r k_e + \varepsilon_r k_p}, \quad (1e) \]

for p-polarized light, where \( \varepsilon_i \) and \( d_i \) are the dielectric constant and the thickness of the \( i \)th medium \((i = 1, 2, 3, \text{and } 4)\) correspond to the prism, the air, the film, and the substrate, respectively, \( \theta_i \) is the angle of incidence at the first interface, \( \omega \) is the frequency, and \( c \) is the speed of light. In the theoretical calculations, we used fixed values for the dielectric constants of prism \((\varepsilon_1 = 5.76)\) and air \((\varepsilon_0 = 1.00)\). The thickness of the Ti_{1-x}Nb_{x}O_2 thin film was \( d_3 = 100 \text{nm} \), and that of the air \( d_4 \) was a variable parameter. Note that \( d_4 \) affects only the depth of the dip and does not affect the position and width of the dip. The real \((\varepsilon')\) and imaginary \((\varepsilon'')\) parts of the dielectric constants of Ti_{1-x}Nb_{x}O_2 were given by the function consisting of a Lorentz term and a Drude term as follows:

\[ \varepsilon = \varepsilon_0 \left[ 1 + \frac{\omega_0^2}{\omega_0^2 - \omega^2 + i \gamma_0 \omega} \right], \quad (2a) \]

\[ \varepsilon_0 \text{Lorentz} = \frac{f_c \omega_0^2}{\omega_0^2 - \omega^2 + i \gamma_0 \omega}, \quad (2b) \]

\[ \varepsilon_0 \text{Drude} = \frac{\omega_0^2}{\omega^2 + \gamma_0^2} - \frac{\gamma_0^2 \omega_0^2}{\omega(\omega^2 + \gamma_0^2)}, \quad (2c) \]

where \( f_c \) is the oscillation strength, \( \omega_0 \) the transition frequency of phonon, \( \gamma_0 \) the loss due to phonon excitation, and \( \varepsilon_0 \) the background permittivity. Plasma frequency \( \omega_p \) and damping factor \( \gamma_p \) are described as a function of \( n \) and \( \mu \), respectively, as follows:

\[ \omega_0 = \sqrt{\frac{mq^2}{\varepsilon_0 n^2}}, \quad (2d) \]

\[ \gamma_p = \frac{q}{m^* \mu}, \quad (2e) \]

where \( q \) is the absolute value of charge of electron, \( \varepsilon_0 \) is the permittivity of free space, and \( m^* \) is the effective mass of electron.

The theoretical reflectance spectra calculated for the Ti_{1-x}Nb_{x}O_2 thin films with \( x = 0 \) and 0.03 are shown in Figs. 2 (c) and 2 (d), respectively. The parameters for the calculations are summarized in Table 2, where \( n \) and \( \mu \) values are taken from the Hall measurement.

We set \( \varepsilon_0 = 9.0, d_2 = 300 \text{nm} \) and \( m^* = 0.5 \times m_e \) \( (m_e: \text{mass of electron} = 9.11 \times 10^{-31} \text{kg}) \). A Lorentzian function was used to calculate the dielectric function of the substrate (LAO). The calculated spectra are similar to the measured ones, indicating that the dielectric constants of Ti_{1-x}Nb_{x}O_2 in this frequency region are well described by the model consisting of a Lorentz term and a Drude term.

Figs. 3 (a) and (b) display \( \varepsilon' \) and \( \varepsilon'' \) of the Ti_{1-x}Nb_{x}O_2 thin films \((x = 0, 0.03)\) as a function of wavelength. For the film with \( x = 0 \), \( \varepsilon' \) is positive at all frequencies of calculation, meaning that this film is a dielectric. In contrast, for the film with \( x = 0.03 \), there is a crossover point at 2.78 \( \mu m \) where the value of \( \varepsilon' \) becomes zero, indicating that the present thin film acts as a metal at wavelengths longer than 2.78 \( \mu m \). Comparison of the \( \varepsilon' \) values for Ti_{1-x}Nb_{x}O_2 thin film \((x = 0.03)\) with that for ITO in literature\(^\text{31}\) \((n = 1.23 \times 10^3 \text{cm}^{-1}, \mu = 40.6 \text{cm} \text{V}^{-1} \text{s}^{-1} \varepsilon_0 = 3.8, m^* = 0.38 \times m_e, \text{crossover point} = 1140 \text{nm})\) reveals that the wavelength of the crossover point for Ti_{1-x}Nb_{x}O_2 thin film with \( x = 0.03 \) is much longer than that of ITO, although \( n \) is similar to one another. This is due to the difference in \( \varepsilon_0 \). A high \( \varepsilon_0 \) of Ti_{1-x}Nb_{x}O_2 \((\varepsilon_0 = 9.0)\) shifts the crossover to longer wavelength.

One interesting property of Ti_{1-x}Nb_{x}O_2 is transport anisotropy. In contrast to other conventional transparent conductive oxides with isotropic s-orbital-dominated conduction bands, the conduction band of Ti_{1-x}Nb_{x}O_2 is mainly composed of anisotropic Ti 3d orbitals. Thus the electrical transport in Ti_{1-x}Nb_{x}O_2 is anisotropic with different crystallographic orientation. Electron mass is \( 0.5 \times m_e \) along the \( a'\)-axis, while it is 3–6 times heavier along \( c'\)-axis\(^\text{34}\). Such mass anisotropy leads to anisotropy in dielectric function.
and crossover point. This creates the frequency region where the sign in $\epsilon'$ is opposite depending on the propagation direction, i.e., the material is either metallic or dielectric, depending on the propagation direction of light. Such materials are called hyperbolic metamaterial (HMM), which shows exotic optical behavior such as negative refraction. While artificial HMM can be made as composites of metal and dielectric patterned on a subwavelength scale, there are few naturally-available, single phase HMM, such as bismuth, boron nitride, and graphite. Ti$_{1-x}$Nb$_x$O$_2$ can be a HMM in IR composed of a single phase.

**4 Summary**

In this study, we have carried out FT-IR reflectance spectroscopy for epitaxial Ti$_{1-x}$Nb$_x$O$_2$ thin films grown on LAO substrates. The variable-angle reflectance spectra for the $p$-polarized light show a clear dip around 1320 cm$^{-1}$ due to photon-to-SPP energy conversion. We calculated the theoretical reflectance spectra by using the Fresnel model of four-phase system, where the dielectric function of Ti$_{1-x}$Nb$_x$O$_2$ was assumed to be the combination of a Lorentz term and a Drude model of four-phase system, where the dielectric function of Ti$_{1-x}$Nb$_x$O$_2$ was negative depending on the propagation direction, $\varepsilon'$ being opposite depending on the propagation direction, $\varepsilon'$ is negative depending on the propagation direction, $\varepsilon'$.

**Acknowledgments**

A part of this work was supported by Kyoto University Nano Technology Hub and NIMS Nanofabrication Platform in the “Nanotechnology Platform Project” sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Financial support from Grant-in-Aids for Scientific Research (B, No. 16H04217) by MEXT is acknowledged. SM is grateful for the support from the construction project for the consortium of the fostering of science and technology personnel, “Nanotech Career-up Alliance (Nanotech CUPAL)”

**References**

Preparation of Nb-doped Anatase Type TiO2 Epitaxial Thin Films and Excitation of Surface Plasmon Polaritons


