Optical and Electric Properties of Nb-doped Anatase TiO₂ Single Crystal

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Abstract

Nb-doped anatase TiO₂ single crystal has been grown by chemical vapor transport method. Raman spectra show that the obtained crystal with Nb of 0.08 wt% has typical anatase structure. An absorption band was observed at around 2.2eV, which seems to be due to the d-d transition in the conduction band. The electron paramagnetic resonance and electric resistivity measurements show that the doped niobium makes quite shallow donor level whose orbital is d_{xy}-like centered at the titanium position of anatase.

Keywords

A. oxides, B. crystal growth, D. electrical properties, D. optical properties,

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1. Introduction

Titanium dioxide is a material used in a wide range of common and high technique applications because of its moderate price, chemical stability and non-toxicity. Recent topical application is a photocatalyst. It is well known, however, that its electrical and optical properties are dominated easily by oxygen vacancies or impurities. It is highly desirable to chemically incorporate impurity atoms without changing the crystallographic structure. Under ambient condition, four structural modifications for titanium dioxide are known: rutile, anatase, brookite and srilankite [1, 2]. The last form is known as α - PbO_2 -type TiO_2 or TiO_2 -II. They are composed of TiO_6 octahedra, but differ from each other by a distortion and coordination of the octahedra. Among these modifications, rutile is the most stable and also the most studied for single crystal, thin films and ceramics. On the other hand, little studies on anatase single crystal have been done compared to thin films and ceramics. The reason is the difficulty of obtaining synthetic single crystals large enough to measure physical properties. Some years ago, we succeed to grow anatase single crystals. Our studies on anatase single crystal [3, 4] reveals that optical properties of anatase largely depend on oxygen vacancies and hydrogen impurities. On the other hand, many impurities have been added into TiO_2 to improve its electrical and optical properties depending on its applications. There are few reports for impurity-doped anatase single crystal. Some extrinsic metal impurities having different valence from titanium attract interest of us. The aim of this study is to obtain Nb-doped anatase titanium dioxide single crystal and to elucidate a behavior of the doped carriers.

1. Experimental

Niobium-doped anatase single crystals were grown by the chemical vapor transport (CVT) method. It is recommended for growing anatase single crystals to use titanium dioxide powder of rutile phase as raw material. In order to suspend niobium uniformly in single crystal, it seems to be one of the advantageous methods to use solid solution. We heated a mixed powder of high purity NbO_2 and TiO_2 (5:95) in a silica glass ampoule at 1000 °C for 12 hours. The x-ray powder diffraction reveals that the resultant powder was a single phase of rutile solid solution and the increment in lattice volume was 0.5 percent. The solid solution powder was added into the TiO_2 rutile powder at a desired composition and they were sealed in a silica glass ampoule with a transport agent (NH_4Cl). The temperatures of the source and growing zones were 750-800 and 650-700 °C within ± 1 °C, respectively. They were kept for 2-3 weeks. Figure 1 shows that the resultant products penetrated into the wall of the glass ampoule. Some of them

have a truncated trigonal-prism shape with a dark blue color and transparency. The niobium content was determined to be 0.08 wt% by an emission spectrometer using inductively coupled plasma, which was performed by The High Purity Chemicals Laboratory Co. Ltd.

Temperature dependence of resistance of one of Nb-doped crystal with $3.0 \times 1.0 \times 0.4 \text{ mm}^3$ in size was measured by the four probe method at a direct constant current of 1 mA. Polarized Raman spectra were measured at the room temperature in back-scattering configuration with a single-monochromator (HR-460, Horiba) and Ar ion laser (GLG-3260J, NEC) as an exiting light source. The narrow-band holographic rejection filter was employed to cut off the Rayleigh scattering light. Polarized optical absorption was measured at desired temperatures in the same way as previously used [3]. The crystal was polished to have (010) face with thickness 0.740 mm before these optical measurements.

Electron paramagnetic resonance (EPR) spectra were recorded using Bruker ESP300E spectrometer equipped with ER041XK microwave unit operating at X-band frequency (9.445 GHz) and ER035M gauss meter. The Oxford GFS600 cryostat was employed for low temperature measurement at 5 K. The moderate amplitude of the modulation was set in order to obtain suitable line shape. The size of the crystal and a power of the microwave were optimized, where the saturation should not be observed in the recorded spectra.

2. Results and Discussion

The polarized Raman spectra shown in Fig. 2 indicate that the product is anatase single crystal. The factor group analysis of the tetragonal primitive unit cell of anatase gives 15 optical modes with the following irreducible representation of normal vibrations: $1A_{1g} + 1A_{2u} + 2B_{1g} + 1B_{2u} + 3E_g + 2E_u$. The modes of A_{1g} , B_{1g} and E_g are Raman active. The frequencies of the Raman bands agree with those in previous study [5]. In the Y(ZX)Y configuration, three E_g modes are selectively observed at 143.4, 196.9 and 637.6 cm^{-1} , which satisfies symmetrical consideration. In the Y(XX)Y configuration, intense bands at 395.5 and 516.1 cm^{-1} are assigned to B_{1g} , and $A_{1g} + B_{1g}$ modes, respectively. The latter band at 516.1 cm^{-1} is a doublet of A_{1g} , and B_{1g} modes which can resolved at low temperature [5]. The appearance of the small band belonging to the E_g mode in this configuration is due to our misorientations in the measurement. The spectra are typical of anatase without any feature due to the other phases such as rutile, brookite and srilankite [6-9]. These show that the grown crystal has a good quality.

Figure 3 shows temperature dependence of resistivity of Nb-doped crystal which is the order of 10^{-2} - 10^{-3} Ωcm . It is believed that the doped niobium replaces titanium in anatase. Niobium has one additional valence electron compared to titanium, and it will make donor level in the band gap. If all of the doped niobium releases its redundant electron to conduction band, the maximum carrier (electron) density can be estimated to be the same as the niobium density. The density of niobium can be calculated easily using the analytical value of niobium content and the density of anatase, 3.90 g/cm^3 . The calculated value is $2.0 \times 10^{19} \text{ cm}^{-3}$. The resistivity for the Nb-doped crystal shown in Fig. 3 is smaller than that for undoped anatase in which the carrier density is less than 10^{18} cm^{-3} [10]. At low temperatures of 4-70 K, the resistivity of the Nb-doped crystal increases with decreasing temperature but the ascending rate is much smaller than that of the undoped one. In a common extrinsic semiconductor, the resistivity exponentially increases with decreasing temperature because of the decrease in carrier density. The temperature dependence of the resistivity of Nb-doped crystal suggests that the density of charged carriers changes little at low temperatures. At higher temperatures of 100-300 K, the resistivity increases gradually with increase in temperature. This indicates that almost all carriers are thermally activated to the conduction bands below 100 K. These suggest that the donor level is quite shallow.

Figure 4 shows polarized optical absorption spectra from ultra-violet to visible region, where E and c are the electric field vector of incident light and crystalline axis, respectively. The absorption edge shows anisotropy depending on the crystalline axis. This anisotropy is originated from the selection rule for optical absorption, but their assignment is not clear. The absorption increases in lower energy region than 2.7 eV. A broad absorption A is observed in the lower energy region than 2.5 eV in both polarization configuration. A weak band B is also observed at about 2.2 eV. The dark blue color of the crystal is due to the existence of these absorptions. The absorption band B has little temperature dependence. The resistivity measurement reveals the existence of electrons in conduction bands. The lowest band of conduction band is composed mainly of d_{xy} orbital of titanium atoms [11]. The weak absorption band B seems to be due to the electron transition from the lowest conduction band to other higher bands, which corresponds to d-d transition. The band calculation [11] shows that the energy band composed of d_{yz} , d_{zx} orbitals is located about 2.2 eV higher than the bottom of the conduction band. Temperature dependence of the absorption edge is shown in Fig. 5. The measurement was done at temperatures of 290, 240, 200, 160, 120, 90, 65, 40, 20 and 10 K. The absorption edge at about 3.2 eV shows a blue shift with decreasing temperature but is frozen below 90 K. This behavior is the same as that of

undoped anatase single crystal [12]. In $E \perp c$ configuration, the absorption curve of the doped anatase is superimposed on that of undoped one. While, in $E // c$ configuration, there is an energy difference of 50 meV between the absorption curves of the doped and undoped anatase. It is well-known that absorption edge is influenced considerably by structural fluctuations such as imperfections and impurities. It is revealed that an addition of niobium into anatase has some influence on the energy level.

Figure 6 shows temperature dependence of EPR spectra in first derivative line shape. One asymmetrical band is observed in all temperature range of 10-300 K. The width of the band becomes smaller with decreasing temperature. The asymmetric feature of the signal is due to the skin effect of the conduction electrons. Because of restriction of the microwave field to a thin layer on the surface, diffusion of the conduction electrons in the skin-layer causes considerable distortion of the line shape [13]. Figure 7 indicates change in g -value at 10 K as a function of angle θ where θ is the angle between the applied magnetic field H and crystalline axis c . A spin under tetragonal symmetry has an angular dependence of $g = \sqrt{g_{//}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta}$. Using

the curve fitting technique, we obtain the resultant values of $g_{//}=1.9615$ and $g_{\perp}=1.9911$. These values correspond to d^1 electron on the lowest conduction band composed mainly of d_{xy} orbital. The components of an axial g -tensor were calculated on the assumption of Ti^{3+} surrounded by oxygen octahedron with D_{4h} symmetry, which were $g_{//}=1.959$ and $g_{\perp}=1.990$ [14, 15]. If the small electric resistivity of Fig. 2 is taken into consideration, these indicate that electrons are still located on the conduction band without falling to donor level due to doped niobium atoms at 10 K. This reveals that the energy difference between the donor level and the lowest conduction band is less than 1 meV. The doped niobium makes a shallow impurity levels in anatase single crystal.

3. Summary

Nb-doped anatase TiO_2 single crystal has been grown by chemical vapor transport method using NH_4Cl as transport agent. The growth of Nb-doped anatase crystals occurs at temperatures of 650-700 °C. The good quality of the crystal is confirmed by polarized Raman scattering measurement. The crystal has a resistivity of the order of 10^{-2} - 10^{-3} Ωcm in temperature range of 4-300 K. In optical absorption, a weak absorption band assigned to d-d transition is observed at 2.2 eV. The absorption edge shifts to higher energy side with decreasing temperature but is frozen below 90 K. The g -value of the conduction electrons are $g_{//}=1.9615$ and $g_{\perp}=1.9911$. The impurity level originated from Nb is quite shallow.

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Fig.1 Examples of Nb-doped anatase single crystals. Crystals were grown on the wall of silica ampoule.

Fig.2 Polarized Raman spectra of Nb-doped anatase single crystal. The polarized scattering configuration is conventionally represented by the notation $D^i(P^iP^s)D^s$, where D^i and D^s are the incident and scattered propagation directions, and P^i and P^s are the incident and scattered polarization directions.

Fig. 3 Temperature dependence of resistivity of Nb-doped anatase single crystal. The crystal has a length of 3.33 mm (effective length of 2.33 mm), width of 1.03 mm and thickness of 0.44 mm.

Fig. 4 Polarized optical absorption spectra of Nb-doped anatase single crystal at 300, 77 and 5 K, where $\mathbf{E}$ and $\mathbf{c}$ are the electric field vector of incident light and crystalline axis, respectively.

Fig.5 Temperature dependence of optical absorption edge. The dotted curve is absorption of undoped anatase observed at 77 K [4]. In $E \perp c$ configuration, the curve of undoped anatase is superimposed on the curves of Nb-doped one observed below 90K.

Fig.6 Change in X-band EPR spectra of Nb-doped anatase single crystal depending on temperature, where H is the magnetic field vector.

Fig.7 Angular dependence of the EPR signal of Nb-doped anatase single crystal at 10 K. The curve represents the best fit of the equation of $g = \sqrt{g_{//}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta}$ with parameters of $g_{//}=1.9615$ and $g_{\perp}=1.9911$.