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Radiation-induced luminescence from sol–gel anatase TiO_2 by 10 keV O^+ irradiation

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Abstract

Radiation-induced luminescence by 10 keV O^+ ion irradiation has been used to study photon emission from sol–gel derived anatase TiO_2. The visible band at 2.3 eV and the UV band at 3.8 eV were observed. The UV band was excited by direct transitions generated by ion irradiation. Sol–gel anatase TiO_2 reabsorbs the photons with energies higher than the band-gap (3.2 eV) and we suggest it to react as a photocatalyst by ion irradiation.

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Keywords: Ion irradiation; Optical emission spectroscopy; Radiation-induced luminescence; Sol–gel method; Titanium dioxide; Thin film

1. Introduction

Sol–gel methods are widely used for synthesizing inorganic materials, such as glass and ceramics, at low temperature by hydrolysis and polycondensation of the precursor in solution [1]. The sol–gel derived oxide crystals include numerous defects introduced during processing. These defects can be reacted as an energy absorber and a photon emitter under ion irradiation.

Titanium dioxide (TiO_2) has a possibility for the use in a variety of applications as a functional inorganic material, such as a photocatalyst [2,3]. The most popular crystal forms of TiO_2 are rutile (band-gap 3.0 eV) and anatase (3.2 eV). Rutile excels in the visible light response, since the photoabsorbability is more effective than that of anatase. On the other hand, anatase is superior to rutile for

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the activity of photocatalysis that increases in proportion to the band-gap. The photocatalysis of TiO_2 progresses under solar irradiation. It may also appear by reabsorption of ultraviolet (UV) light or phonon-assisted excitation generated by ion irradiation.

In this paper, radiation-induced luminescence (RIL) spectroscopy of an anatase TiO_2 thin film synthesized by sol–gel method is reported. The in-situ optical emission spectroscopy under ion irradiation was performed to investigate energy transfer. The production processes involved for the observed bands are discussed.

2. Experimental

The TiO_2 specimens were prepared by the sol–gel method. The anatase titania sol (Ishihara, STS-21, particle size 20 nm, specific surface area 50 m^2/g) was well stirred in distilled water. The solution was coated on 20×25 mm substrate using a spin coater, and heated at 400 °C for 1 h. The thickness of the prepared TiO_2 film was about 10 μm. An ITO (Indium Tin Oxide, $SnO_2 + In_2O_3$) coated glass was used to give an electrical conductive sheet thereby to preventing a charge build-up by ion irradiation. The thickness of the coated ITO and the backing glass substrate were 0.1 and 1 mm, respectively.

The ion irradiation was performed using an electron cyclotron resonance (ECR) ion source in TIARA, JAERI-Takasaki [4]. Ions were extracted from the source, mass analyzed by a 90-degree magnet and transported into the collision chamber. The base pressure of the beam line was kept at 10^{-5} Pa. The distance from the source to the target specimen was about 3 m.

The crystallographic relationships between the prepared film and the substrate were investigated with a high-resolution X-ray diffractometer (X'Pert-MRD, Philips). The X-ray source was operated at 40 kV and 30 mA for the Cu–Kα line.

For RIL spectroscopy, the light emitted from the specimen was focused into an optical fiber input located at 45° to the normal, 30 cm from the specimen. The interface between the vacuum chamber and air was a non-coated fused silica view port, where the transmittance in the UV region above 5 eV was very low. The spectrometer (Hamamatsu PMA-11) consisted of a thermoelectric-cooling type back-thinned charge coupled device image sensor, a compact Czerny–Turner type spectrograph with F-number 4, an optical fiber probe and a control circuit. The wavelength resolution was less than 2 nm.

3. Results and discussion

Fig. 1 shows the scanning electron microscope (SEM) micrograph of the prepared TiO_2 film on an ITO coated glass substrate. There are various particles of micrometer size on the surface, and the film appears milky due to light scattering. The surface structure is not influenced by the backing glass substrate (thickness ~1 mm) and ITO coat (~0.1 mm), since the TiO_2 film (~10 μm) is sufficiently thick.

Fig. 2(a) and (b) show the XRD patterns of the TiO_2 specimen and the ITO coated glass substrate, respectively. The pattern of the TiO_2 specimen in Fig. 2(a) includes that of the substrate, since X-rays penetrate easily the specimen. The peaks in Fig. 2(b) correspond to those originating from the ITO coated glass. Therefore the peaks except for them correspond to those originating from the TiO_2 film. The calculated d spacings in Fig. 2 are corresponding to the peaks of the anatase crystal form [5].

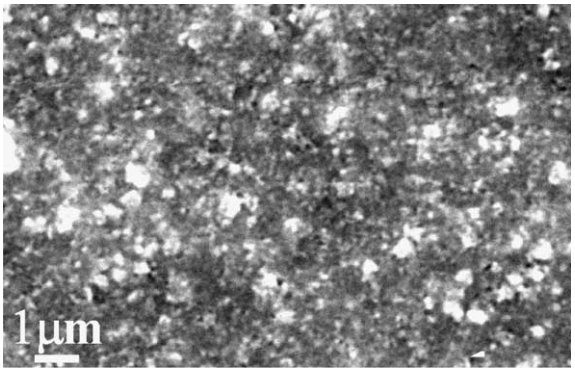

Fig. 1. SEM micrograph of the TiO2 thin film prepared by sol–gel method.