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Electron beam irradiation-induced reduction of Sn on epitaxial rutile $Sn_xTi_{1-x}O_2$ alloy thin films

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ABSTRACT

Epitaxially-grown $Sn_xTi_{1-x}O_2$ alloy thin films with different compositions were fabricated by successive deposition of SnO_2 on ultra-smooth Nb-doped TiO_2 (rutile) (110) substrates. The surface Sn atoms of the $Sn_xTi_{1-x}O_2$, which took a tetravalent state just after the deposition under the present condition, were reduced into a metallic state by electron beam irradiation, but not for a pure SnO_2 film. The reduction process approximately obeys zero-order kinetics; the reaction rate constant linearly increases with an increase of the surface composition of Ti. Based on these results, the reduction mechanism is discussed.

1. Introduction

TiO_2 and SnO_2 are representative oxides to take a crystal structure of rutile; it is known that they can form a solid-solution each other in bulk, although depending on the temperature and process they sometimes exhibit nano-scale spinodal decomposition, *i.e.* the phase separation with a periodic modulation of its composition [1–3]. Therefore, this SnO_2–TiO_2 system has been well examined in bulk ceramics. On the other hand, their single crystal surfaces have been intensively studied as a model system to get a general understanding of catalytic properties on oxide surfaces [4–8], while the SnO_2–TiO_2 alloy surface has not been yet. It is because each pure single crystal is commercially available, but not is the single crystal alloy of SnO_2–TiO_2. However, the SnO_2–TiO_2 alloy has some possible applications such as gas sensors [9–11] and photocatalysts [12,13]. Both of these characteristics are related to phenomena very sensitive to the surface/interface properties. From these points of view, it would be thus also important to investigate the surface and the interface of the SnO_2–TiO_2 alloy system.

For this purpose, we need a single crystalline of the SnO_2–TiO_2 alloy, to which one of the best solutions is to employ a pulsed laser deposition (PLD) method for well-defined epitaxial SnO_2–TiO_2 alloy films. Recent progress in oxide epitaxy now enables us to grow single crystalline oxide films with high-quality. Especially for rutile TiO_2 and the related rutile compounds, are available atomically flat TiO_2 single crystal substrates that have been originally developed by our group [14]. In this study, we fabricated SnO_2–TiO_2 films by means of successive deposition of the SnO_2 on Nb-doped TiO_2 (rutile) (110) single crystal substrates by PLD at high temperatures enough to cause intermixing of the SnO_2 overlayer and the underlying TiO_2 substrate; the surface composition and structure were examined step by step with *in situ* Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), as well as with *ex situ* X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). As a result, we found a phenomenon of electron beam irradiation-induced reduction of Sn atoms on the SnO_2–TiO_2 alloy thin film surfaces.

2. Experimental details

Experiments were carried out in an ultra high vacuum PLD chamber equipped with *in situ* surface characterization of AES and LEED. The base pressure was 6.7×10^{-7} Pa in the PLD chamber and 2.7×10^{-8} Pa in the analysis chamber, respectively. SnO_2 or $Sn_{0.5}Ti_{0.5}O_2$ targets were ablated by KrF excimer laser ($\lambda = 248$ nm, ~1 J/cm^2, 1 Hz) to fabricate epitaxially-grown SnO_2 or SnO_2–TiO_2 films on ultra-smooth Nb-doped (0.05 wt.%) TiO_2 (rutile) (110) substrates. The optimum growth condition for high-quality SnO_2 and SnO_2–TiO_2 films was substrate temperature 700 °C, deposition rate 6×10^{-3} nm/pulse and oxygen partial pressure 1.3 Pa, respectively; especially the high oxygen partial pressure is a key for Sn to be completely oxidized in the film. Thus, in order to obtain an enough conductivity of the samples for AES and LEED measurements, the Nb-doped substrates were intentionally used in the present experiment.

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The experimental procedure is summarized as follows. SnO_2 layers were sequentially deposited on the substrate by PLD with the SnO_2 target in steps of 100 pulses. Each film surface was examined in detail with LEED and AES and it was then followed by the electron beam reduction experiment. The primary electron beam energy was 3 keV in AES. For the electron beam irradiation-induced reduction experiment, the AES electron beam was also used; the backpressure was kept under 2.7×10^{-7} Pa during the irradiation. SnO_2–TiO_2 films were also deposited directly from the $Sn_{0.5}Ti_{0.5}O_2$ target with 1500 pulses at which the effect of interlayer diffusion may be negligible for such a thicker $Sn_{0.5}Ti_{0.5}O_2$ film. After all the *in situ* experiments, the film samples were once taken out in air and then *ex situ* analyses with XPS and XAS were performed for some of these samples at BL2C of the Photon Factory, High-Energy Accelerators Research Organization (KEK). The XAS spectra were taken by the total-electron-yield method. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows a change of the Auger peak height ratio of 424 eV Sn peak to 383 eV Ti peak for SnO_2 deposited on the Nb-doped TiO_2 (110) substrate as a function of the laser pulse number. Note that the deposition rate is about 6×10^{-3} nm/pulse in this experiment. At the beginning of the SnO_2 deposition, taking the effective attenuation length of Ti LMM Auger electron (less than 1 nm) into account, for the amount of the SnO_2 deposited, the Auger peak height ratio did not increase so rapidly as would be expected for the growth in a layer-by-layer fashion. One possible interpretation for this behavior of the Auger peak height ratio is often that the film grows in a 3D-island growth mode, but this is probably not the case. It is because although it was a different experiment in another chamber system with STM, the film surface was found to exhibit a step and terrace structure at the initial stage of the deposition as observed by scanning tunneling microscopy (STM) (not shown). Since TiO_2 and SnO_2 forms a solid-solution in bulk, it is rather expected that the SnO_2 over-layer and the underlying substrate of TiO_2 can diffuse one to another at their interface to form a $Sn_xTi_{1-x}O_2$ alloy thin layer under the present growth temperature as high as 700 °C. In fact, it is reported [15] that a similar rapid diffusion process of Sn into the TiO_2 substrate occurs to form $Sn_xTi_{1-x}O_2$ solid solutions at high growth temperatures. The rapid increase of the Auger peak height ratio observed above the number of the laser pulse of 400, corresponding to 2.4 nm in thickness might be due to the limit of their diffusion ability.

This speculation is also supported by the appearance of a new surface reconstruction particular to the present SnO_2–TiO_2 film surfaces. Fig. 2(a) is a LEED pattern for a clean (1×1) TiO_2 (110), and the subsequent of (b)–(d) is those for different amounts of SnO_2 deposited with laser pulses of 200, 400 and 700, respectively. The SnO_2-deposited surfaces basically showed a (1×1) structure similar to that of the TiO_2 (110), indicating that the obtained films were epitaxially grown on the substrate. When the number of the laser pulse is 200, there appeared short streaks running along the <001> direction in the LEED pattern, as shown in Fig. 2(b). There is no report on the observation of a similar short streak along the <001> direction on either TiO_2 (110) or SnO_2 (110) single crystal surfaces in the present oxidizing condition. This is therefore a good indication for the formation of $Sn_xTi_{1-x}O_2$ alloy thin films. In fact the streaky (1×1) pattern could be observed also for thicker $Sn_{0.4}Ti_{0.6}O_2$ alloy films deposited directly from the $Sn_{0.5}Ti_{0.5}O_2$ target under the same growth condition.

In general, little information of the chemical state can be taken from AES, but there are a few exceptional cases where the peak position shifts depending on the chemical state. In fact, the Sn MNN peaks are this case, *i.e.* the peaks for divalent and tetravalent states are located at 425.5 and 432.5 eV, while at 430 and 437 eV for a pure metal state [16,17]. In Fig. 3 (a), is shown a set of Auger spectra for the SnO_2-deposited surface (300 pulses) taken with time in a narrow kinetic energy range of 400 to 450 eV, for looking at the Sn MNN peak positions in more detail. In the first measured spectrum, the Auger peak can be assigned to the non-metallic state of Sn; finally the chemical state of Sn was determined to be the tetravalent state by *ex situ* XPS (not shown) as well as and XAS (not shown). During a long exposure of the primary electron beam in AES measurement, the initial peak intensities gradually decreased and a set of additional peaks simultaneously appeared, which can be assigned to the metallic state of Sn, accompanied by a systematic reduction of the Auger peak intensity of O KLL as shown in Fig. 3(b). This result indicates that the surface Sn was efficiently reduced into metal by electron beam irradiation. The resultant metallic Sn atoms are probably segregated to

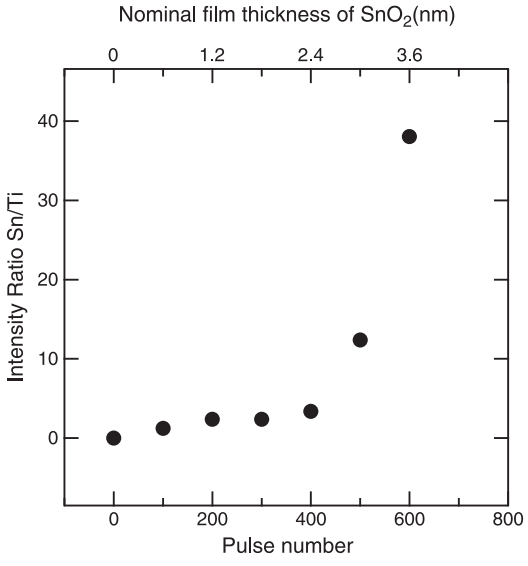

Fig. 1. Auger peak height ratio of 424 eV Sn peak to 383 eV Ti peak plotted as a function of the laser pulse number of SnO_2 deposited on the Nb-doped TiO_2 (110) substrate.

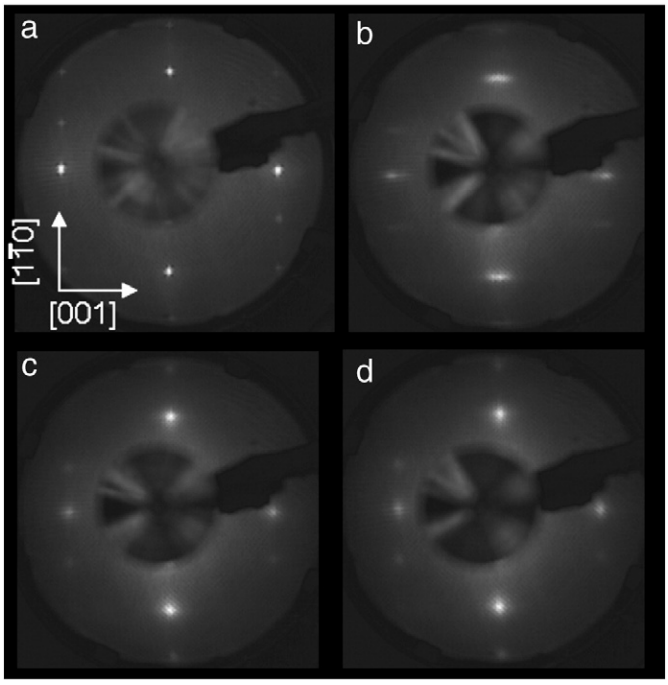

Fig. 2. (a) LEED pattern for a clean (1×1) TiO_2 (110), and the subsequent of (b)–(d) for different amounts of the SnO_2 deposited with laser pulses of 200, 400 and 700, respectively. (Ep = 78 eV).