



Aqueous phase deposition of dense tin oxide films with nano-structured surfaces



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ABSTRACT

Dense tin oxide films were successfully fabricated in an aqueous solution. The pH of the solutions was controlled to pH 1.3 by addition of HCl. Precise control of solution condition and crystal growth allowed us to obtain dense tin oxide films. Concave–convex surface of fluorine-doped tin oxide (FTO) substrates was entirely-covered with the continuous films. The films were about 65 nm in thickness and had nano-structured surfaces. Morphology of the films was strikingly different from our previous reported nano-sheet assembled structures. The films were not removed from the substrates by strong water flow or air blow to show strong adhesion strength. The aqueous solution process can be applied to surface coating of various materials such as nano/micro-structured surfaces, particles, fibers, polymers, metals or biomaterials.

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1. Introduction

Tin oxide is one of the promising materials for future devices [1–11]. It has been applied to gas sensors [12,13], optical devices [14], lithium batteries [15–17], dye-sensitized solar cells, molecular sensors or optoelectronic devices. Recently, aqueous solution processes were developed to prepare metal oxides [18,19] such as SnO₂ [20–25], TiO₂ [26] or ZnO [27]. SnO₂ nano-sheet assembled structures were developed for molecular sensors or cancer sensors [28]. The nano-sheet was one of the ideal structures to increase surface area. High surface area directly affected sensing property. Surface relief structure and continuous open pores were suitable to flow reaction solution. High photocurrent and high signal-to-noise ratio were obtained from the sensors. The SnO₂ nano-sheet assembled structures had hydrophilic surfaces. They were modified to super-hydrophilic surfaces with light irradiation [28,29]. However, reported SnO₂ structures were limited. Novel aqueous solution processes should be developed to fabricate various nano/micro-structures. Especially, coating technology of concave–convex surfaces with dense SnO₂ crystal films is strongly required for conductive electronic devices, optical devices or anticorrosion coatings. Fluorine-doped tin oxide (FTO) substrates have been widely used in electronic devices or optical devices as transparent conductive substrates. They had typical concave–convex surfaces of SnO₂ polycrystals. Transparent conductive substrates with high surface area were required for

sensors or solar cells. On the other hand, flat surfaces were needed for electronic devices. Control of surface morphology was strongly required to improve performance of devices. In this study, concave–convex surfaces of FTO substrates were coated with dense continuous films with surface nano-structures. Morphology control of the tin oxide films was achieved with precise control of crystal growth.

2. Synthesis of dense tin oxide Films

Hydrochloric Acid solution (HCl, 1 N, 1 mol/l, NACALAI TESQUE, Inc., Kyoto, Japan) of 20 ml was added to hot distilled water of 180 ml at 90 °C. Tin fluoride powder of 870.6 mg was dissolved in the aqueous solution. Concentration of tin fluoride was 25 mM.

Fluorine-doped tin oxide (FTO) layers were formed on glass plates. FTO layers were polycrystals of SnO₂. They had concave–convex surfaces. Size of the FTO substrate was 26 × 50 × 1.1 mm (Asahi glass Co., Ltd.). They were irradiated with vacuum ultraviolet light for 20 min in air (VUV, low-pressure mercury lamp PL16-110, air flow, 100 V, 200 W, SEN Lights Co.). The FTO substrates were immersed in the tin fluoride solutions 90 °C for 24 h.

Chemical reaction to form SnO₂ is described as follows [28]. SnO₂ is formed though several reaction routes, since tin and other ions form several complexes and species. A dominant route is shown as follows. Valence of tin ion is shown in equations, because it is important to understand oxidation and formation of tin oxides.



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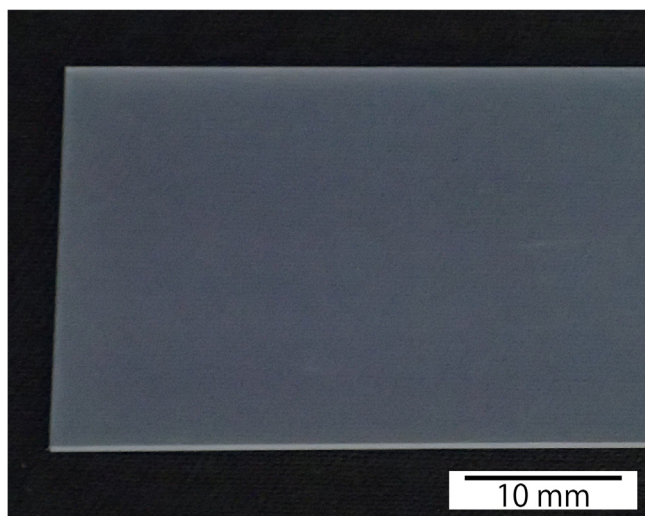
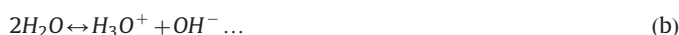


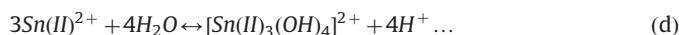
Fig. 1. A photograph of the thin film prepared in the SnF₂ solution of 25 mM at pH 1.3 at 90 °C for 24 h.



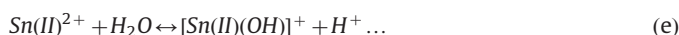
[30]



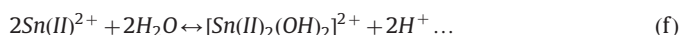
It is known that oxonium-ion is dominant rather than proton in aqueous solutions (Eq. (b)) [30]. Proton is, however, used in equations



[31]



[31]

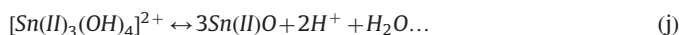
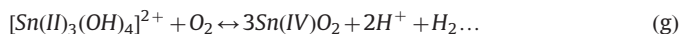


[31]

Multinuclear complex of $[Sn(II)_3(OH)_4]^{2+}$ in Eq. (d) is formed with small amount of $[Sn(II)(OH)]^+$ in Eq. (e) and $[Sn(II)_2(OH)_2]^{2+}$ in Eq. (f) [30].

Multinuclear complex of $[Sn(II)_3(OH)_4]^{2+}$ is circular ion [30]. It is known to be a crystal nucleus of several types of basic tin salts in aqueous solutions at low pH [30].

SnO₂ or SnO is formed from these complexes. A typical route from $[Sn(II)_3(OH)_4]^{2+}$ is shown as follows.



Sn²⁺ ion is known to be easily oxidized to Sn⁴⁺ by dissolved oxygen in the aqueous solutions (Eqs. (g) and (h)) [30]. Especially, oxidation of Sn²⁺ ion progresses rapidly in a dilute SnF₂ solution below 0.5 M [32], since it contains enough oxygen.

SnO is formed from the complex in Eqs. (i) and (j).

SnO is reported to be oxidized to SnO₂ due to its instability as shown in Eqs. (k) and (l).

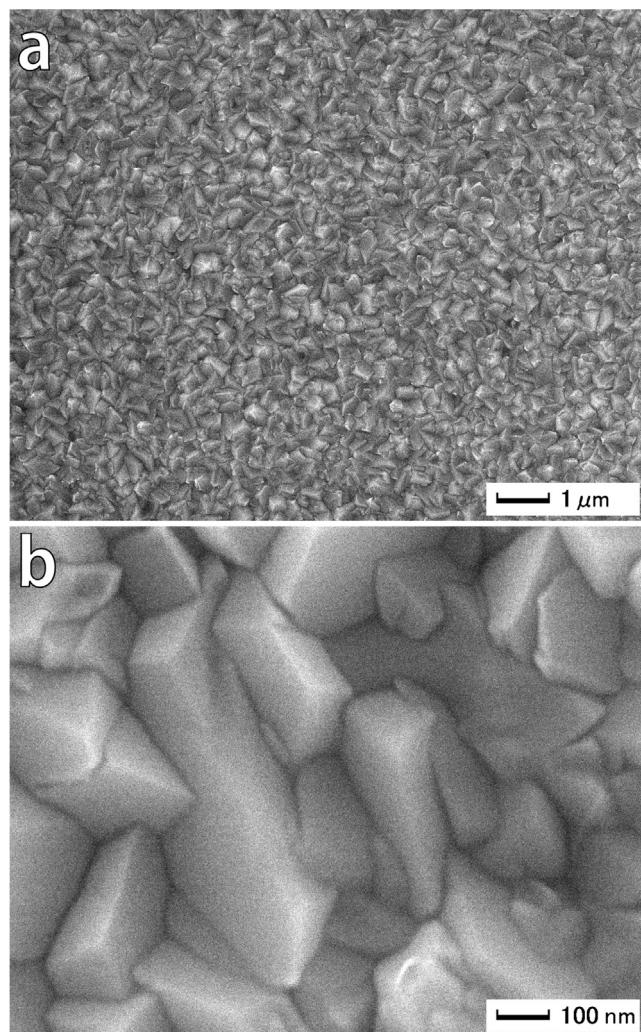
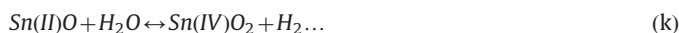


Fig. 2. (a) SEM micrograph of the bare FTO substrate. (b) Magnified area of (a) showing surfaces of SnO₂ polycrystals.

[31,33]



Moreover, SnO₂ or SnO is formed from $[Sn(II)(OH)]^+$ in Eq. (e) or $[Sn(II)_2(OH)_2]^{2+}$ in Eq. (f) similarly.

Surface of the films was observed with a field emission scanning electron microscope (FE-SEM; JSM-6335FM, JEOL Ltd.). Fracture cross-section of the films was observed with the FE-SEM. The films were evaluated with an X-ray diffractometer (XRD; RINT-2100V, Rigaku) with CuK α radiation (40 kV, 30 mA). Transparency and reflectance of the films were evaluated with a spectrophotometer (UV-VIS-NMR; V670, JASCO Co.). Light was induced from FTO side of the substrates for both transparency evaluation and reflectance evaluation.

It was notable that pH of the solutions was different from that in our previous reports [20–25]. It caused difference in morphology of SnO₂. The pH of HCl solution was about 1.24. It changed to about 1.31 by addition of SnF₂. The solutions were transparent. In contrast, the solutions became clouded just after dissolution of SnF₂ in our previous reports because SnO₂ particles were generated homogeneously. Supersaturation degree was controlled to enough low to suppress homogeneous nucleation with pH adjustment in this study. Acid condition decreased crystal growth speed of SnO₂. It allowed us to obtain continuous thin films. The pH of the solutions was about 1.37 after 24 h. It slightly increased by progress of above chemical reactions.

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