Nature of dark-brown SnO₂ films prepared by a chemical vapor deposition method

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We recently found dark-brown SnO₂ films were formed in a chemical vapor deposition process under a limited oxygen supplying condition and the nature was investigated in this work. Those films were deposited from SnCl₂ at 350–600 °C in a tubular furnace. The films had the rutile-type structure with the significant preferred-orientation along <1 0 0> normal to the substrate surface. Thermogravimetric and elemental analyses revealed that the oxygen deficiency (VO) and Cl contamination occurred in the films. An as-deposited film at 350 °C contained V₀ of 1.5 × 10²¹ cm⁻³, which corresponded to that about 2.5% was vacant in the O site. On the other hand, Cl was contained at 7.4 × 10²⁰ cm⁻³ in the 350 °C-prepared film. The Cl concentration decreased with deposition temperature and became 1.8 × 10²⁰ cm⁻³ at 600 °C. The films showed moderate electric conductivity and the film deposited at 500 °C had the lowest resistivity of 2.5 × 10⁻² Ωcm, where the carrier density and the Hall mobility were 1.3 × 10²⁰ cm⁻³ and 2.0 cm² V⁻¹s⁻¹, respectively.

Key-words : SnO₂, Chemical vapor deposition, SnCl₂, Oxygen vacancy, Chlorine contamination

1. Introduction

The band-gap energy of tin dioxide (SnO₂) is 3.89 eV (at 27°C)¹ and ‘ideal’ crystals should be an insulator. However, real crystals show n-type semiconductivity because of the native defects. SnO₂ has been used for a transparent electrode (TE) material because of the coexistence of transparency and electric conductivity. SnO₂-based TE is the most prototypic and, currently, indium-tin-oxide (ITO) is the most popularly used for TE in practice. On the other hand, indium is a rare element and imbalance between the increasing demand and the limited supply is becoming a problem. SnO₂-based TE is still important as an alternative of ITO.

The electric conductivity of SnO₂ strongly depends on the preparation conditions and is usually enhanced by reducing treatment. The defect types which crucially affect the conductivity are not determined yet but oxygen vacancy (V₀) has been believed to be responsible for the electric conductivity in unintentionally doped SnO₂. On the other hand, recent studies suggested that V₀ is not a shallow donor.²⁻⁴ Rather, other defects such as interstitial tin and defect complexes were proposed.⁵⁻⁶ Substituting Sn⁴⁺ with penta-valent cations such as Sb⁵⁺ and/or O²⁻ with mono-valent anions such as F⁻ enhance the carrier concentration.⁷⁻⁸ For example, the chlorine contamination is considered to be an origin of the electric conductivity of SnO₂ prepared from tin chloride in CVD processes.⁹⁻¹⁰ Agashe et al. reported that doping Cl⁻ or Br⁻ increased the electric conductivity of SnO₂ films prepared in a spray pyrolysis process but the heavy doping degraded the conductivity again.¹¹⁻¹² However, the Cl concentration was not shown in their papers and there are few reports that described the detailed effects of Cl doping.

SnO₂ is optically ‘transparent’ as mentioned above but we recently found that dark-brown SnO₂ was prepared from SnCl₂ in a CVD process under a restricted oxygen-supplying condition. Coloring is not preferable for TE application but the investigation on the origin of coloring will bring useful knowledge which leads to improvement of the performance. These dark-brown films show relatively high electric conductivity and have some interesting features such as preferred orientation on the glass substrates. In this work, the nature of dark-brown SnO₂ is investigated.

2. Experimental

The CVD apparatus was assembled with an alumina tube and a muffle furnace (Fig. 1). Commercial reagent of SnCl₂ (Kanto Chemical, K. K., 99%) was filled in an alumina boat and a quartz-glass substrate (5 × 10 × 1 mm³) was placed on it (Fig. 1). The boat was put into the furnace and was heated at a temperature between 350 and 600°C. Dry air was flowed at a rate of 20 sccm (standard cubic centimeter per minute) during the deposition. SnO₂ was deposited on the substrate with the following

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reaction.

\[
\text{SnCl}_2(\text{vap}) + \text{O}_2 \rightarrow \text{SnO}_2 + \text{Cl}_2 \quad (1)
\]

The deposition time was set for 10 h at 350°C, 5 h at 400°C, and 1 h at 450°C and above, which were determined at a time when the weight loss of the source \(\text{SnCl}_2\) stopped after the deposition at a given temperature. The melting point of \(\text{SnCl}_2\) is 246°C and the vapor pressure at 350°C is 0.5 kPa. It increases as 1.6 (400°C), 6.0 (450°C), 16.0 (500°C), 38.4 (550°C) and 77.3 kPa at 600°C.\(^{15}\)

The prepared films were characterized by X-ray diffraction (XRD) (Rad-IIb, Rigaku, Japan) with Cu Kα radiation, scanning electron microscopy (SEM) (XL–30, Philips, The Netherlands), electron-probe micro-analyzer (EPMA) (JXA–8900M, JEOL, Japan), thermo-gravimetric analysis (TG) (Thermo Plus 2, Rigaku, Japan) and visible-light absorption measurements. Hall-effect measurements were carried out to characterize the electric properties with a 0.55 T-electromagnet at room temperature.

3. Results and discussion

3.1 Characterization

The substrates were covered with dark brown films after the deposition. The typical photographic image of a film is shown in Fig. 2. The film on the right-hand side (Fig. 2) was deposited at 350°C and a quartz substrate is shown on the left-hand side for comparison. The deposited film was barely translucent, although it looks opaque in Fig. 2 (right). Figure 3 shows the transmittance spectrum of the as-deposited film at 350°C and the post-annealed at 1000°C for 8 h in O₂. The transmittance is low particularly at the shorter-wavelength region and gradually increases with wavelength. The transmittance was slightly improved by the post heat-treatment and the steep rise related to the band-gap developed near 300 nm. However, the overall transmittance did not exceed 60% even after the annealing.

XRD showed that those dark-brown films had the rutile-type structure without any second phases such as \(\text{SnO}\) and \(\text{Sn}\). Figure 4 shows the XRD patterns of films deposited at 350, 500 and 600°C and commercial \(\text{SnO}_2\) powder for comparison. The XRD patterns of the films resembled each other and all the peaks were assigned to rutile-type \(\text{SnO}_2\) (ICDD #41-1445). The films showed significant preferred-orientation along <1 0 0> normal to the substrate surface and the degree of the preferred-orientation was slightly enhanced with the deposition temperature. The Lotgering’s preferred orientation factor (\(f\)), defined by Eqs. (2) and (3),\(^{16}\) was shown in Fig. 4(b) for the films deposited at the different temperatures.

\[
f = \frac{(P - P_0)}{(1 - P_0)} \quad (2)
\]

\[
P = \sum \frac{I_{hal}}{\sum I_{hkl}} ; \quad P_0 = \sum \frac{I_{000}}{\sum I_{hkl}} \quad (3)
\]

Where, \(P\) and \(P_0\) are the ratio between the intensity sums of the \(h\) 0 0-series reflections and all the \(h\) \(k\) \(l\) reflections. \(P\) is for an oriented sample and \(P_0\) for a randomly-oriented standard-sample. If the sample is completely orientated, \(f\) becomes 1, and \(f = 0\) for

![Fig. 2. Photographic image of dark-brown \(\text{SnO}_2\) film (right-hand side) and quartz substrate (left-hand side).](image)

![Fig. 3. Transmittance spectra of as-deposited film at 350°C and after annealed in O₂ at 1000°C.](image)

![Fig. 4. (a) XRD patterns of films deposited at 350, 500 and 600°C and commercial \(\text{SnO}_2\) powder for comparison. Indices were assigned based on rutile-type \(\text{SnO}_2\) (ICDD #41-1445). (b) Lotgering’s preferred orientation factor (\(f\)) for films deposited at different temperatures.](image)
random orientation. \( f \) is 0.56 for the 350°C-prepared film and monotonically increased with the deposition temperature. It became 0.62 for a film prepared at 600°C. Since the substrate was quartz glass, the preferred orientation of the present films was not caused by a crystallographic relation between the grown films and the substrate like hetero-epitaxy. Such preferred orientation was sometimes observed in SnO\(_2\) films on the glass substrates and that was considered to originate in the preferred growth. Fujimoto et al.\(^{17}\) conducted high-resolution electronic microscopy for a \(<1\ 1\ 0>\) oriented film on the GaAs (1\ 0\ 0) substrate and they concluded that preferred growth took place from the early stage of the growth after the nucleation. Murakami et al.\(^{18}\) suggested that the growth orientation depended not only on the experimental conditions, such as substrate temperature and the degree of supersaturation, but also on the structure of the precursor molecules. They reported that the films prepared from di-\(\alpha\)-butyltin(IV) di-acetate (DBTDA) in a spray pyrolysis method showed preferred orientation along \(<1\ 0\ 0>\) on the glass substrates. On the other hand, tri-butyltin(IV) acetate (TBT) brought \(<1\ 1\ 0>\) orientation. According to them, SnO\(_2\)(g) intermediately produced in the pyrolysis of DBTDA was a possible precursor to bring the \(<1\ 0\ 0>\) oriented SnO\(_2\) films. There is uncertainty as to whether SnO\(_2\)(g) was the sole chemical-species for SnO\(_2\) in the vapor deposition process but the nature of precursors seemed to affect the orientation. The polycrystalline films prepared in spray pyrolysis also tended to show the preferred orientation in various directions as \(<2\ 0\ 0>\), \(<1\ 1\ 0>\) and \(<2\ 1\ 1>\) and it was affected by the starting conditions of the precursors, such as concentration, solvent, additives.\(^{7,8,19–25}\) SnCl\(_2\) used in this work was also a precursor giving rise to the \(<1\ 0\ 0>\) preferred orientation in the CVD process. Interestingly, the films prepared from SnCl\(_2\) solution in an electrospray pyrolysis method didn’t show such preferred orientation, where porous particle-layers were obtained.\(^{26,27}\) The precursor SnCl\(_2\) didn’t pass through the vapor phase to pyrolyze into SnO\(_2\) in the electrospray pyrolysis,\(^{28}\) which was in contrast to that vapor-deposition was normally involved in spray pyrolysis of SnCl\(_2\).

**Figure 5** shows the SEM images of the dark-brown SnO\(_2\) films prepared at 350, 500 and 600°C. Figures 5(a)–(c) show the surface. The films had similar morphology regardless of the depo-
sition temperature. They were composed of densely-packed angular-grains of 1–2 μm and the grain shape became more developed with the deposition temperature (Figs. 5(b) and (c)). The size was the largest at 500°C and smaller grains were observed to be packing between coarse grains at 600°C (Fig. 5(c)). Figures 5(d)–(f) were the cross-sectional view of the films at 350°C, 500°C and 600°C and a columnar structure was characteristic of the films. The thickness increased with the deposition temperature. They were 1.7 μm at 350°C, 3.7 μm at 450°C, 4.4 μm at 500°C, 4.5 μm at 550°C and 5.0 μm at 600°C.

3.2 Compositional analysis

The vapor-deposition reaction of SnCl₂ took place in the tubular furnace where oxygen supply was somewhat limited. Oxygen deficiency was expected in the prepared films. Therefore, TG analyses were performed to estimate the nonstoichiometry. The films were ground into powder for TG and were heated in O₂. Figure 6 shows the weight change of 350°C-prepared films against time. The temperature is also presented in the plot. The result showed that the weight firstly decreased by 0.15 mass% up to 500°C and then increased again above 500°C (Fig. 6). The weight-gain continued after reaching 1000°C and it took 4 h that the weight-gain ceased at 0.36 mass%. Supposing that the weight-gain was solely attributed to the vanishment of the oxygen vacancies, the concentration of V₀ amounted to 1.5 × 10²¹ cm⁻³ in the as-deposited films at 350°C. That value corresponded to that 2.5% of the oxygen sites were vacant. The first weight-loss was probably due to the desorption of adsorbed Cl, for example, on the surface and at grain boundaries.

EPMA semi-quantitative analyses on the dark-brown SnO₂ films exhibited the chlorine contamination on the order of 10¹⁰ cm⁻³ (Fig. 7). The Cl concentration of a film prepared at 350°C was 7.4 × 10²⁰ cm⁻³. The concentration gradually decreased with the deposition temperature and it became 1.8 × 10²⁰ cm⁻³ at 600°C. The post heat-treatment at 1000°C in O₂ for 8 h slightly decreased Cl to 5.0 × 10²⁰ cm⁻³ (shown by an open square in Fig. 7) but this value is still higher than that of the 600°C-prepared film. It suggested that the Cl concentration was mostly determined by the deposition temperature and the Cl-doped Cl was not removed by the post heat-treatment. The contamination level in the present films was comparable to those reported in Ref. 11. 10¹⁰–10¹¹ cm⁻³, 11,14 As a summary of compositional analysis, a film prepared at 350°C has a composition of SnO₁₉₂Cl₀.₀₁₈VO₀.₀₅₄ and tin should have a valence of +3.87 for the charge neutrality. Since the films prepared at 350°C contained Cl at the highest concentration and were expected to be the most oxygen-deficient, the present films were considered to have a composition between SnO₂ and SnO₁₉₂Cl₀.₀₁₈VO₀.₀₅₄.

3.3 Electrical properties

The Hall measurements exhibited that the carrier concentration (n) was the highest at 400°C and was 1.6 × 10²⁰ cm⁻³ (Fig. 7). It decreased with the deposition temperature and became 0.98 × 10²⁰ cm⁻³ at 600°C. Figure 7 shows n together with the Cl concentration. There seems to be a correlation between the Cl and the carrier concentrations at 400°C and above as if chlorine works as an n-type donor. However, TG exhibited that the films contained oxygen vacancy as well on comparable order (1.5 × 10²¹ cm⁻³) in the as-deposited films at 350°C and the contributions to the electric conductivity were not clearly separated between oxygen vacancy and chlorine at the moment.

The Hall mobility (μ) and the resistivity (ρ) are plotted in Fig. 8. The Hall mobility was almost constant as shown in Fig. 8, which results from that the films had similar columnar morphology regardless of the deposition temperature (Fig. 5). The resistivity slightly decreased up to 500°C and then increased again. Films deposited at 500°C had the lowest resistivity of 2.5 × 10⁻² Ωcm. This value was somewhat higher than those typically reported for F-doped SnO₂ by one order of magnitude. It was attributed to the low Hall mobility of the present films. F-
doped SnO$_2$ films prepared through spray pyrolysis had the mobility of 23, which is 10 times larger than that of the present films. The columnar-grain structure probably enhanced the scattering of the carriers at the grain boundaries, because defects such as impurities and dislocation concentrate in the grain boundaries, which may lead to the lower mobility.

Coloring is certainly due to the defects in this material. Blackening was reported in heavily doped SnO$_2$ with antimony in the previous literature, which was explained by the charge-exchange effect among antimony atoms with different charge states, in films. The columnar-grain structure probably enhanced the scattering and the Hall mobility were 1.3 cm$^2$ V$^{-1}$s$^{-1}$. It was possible that both of Cl and...the mobility.

4. Summary

Cl-doped, oxygen-deficient SnO$_2$ was prepared from SnCl$_2$ in the CVD process and the films deposited at the different temperatures exhibited basically similar properties. Those films were colored in dark-brown and showed moderate electric conductivity. The films had the preferred orientation along $\langle 100 \rangle$, which was slightly enhanced with the deposition temperature. The contamination of Cl came from the source SnCl$_2$ and the concentrations was $7.4 \times 10^{15}$ cm$^{-3}$ in the film deposited at 350°C. The Cl concentration decreased with the deposition temperature and became $1.8 \times 10^{20}$ cm$^{-3}$ at 600°C. The lowest resistivity was attained at 500°C with $2.5 \times 10^{-2}$ Ωcm and, then, the carrier concentration and the Hall mobility were $1.3 \times 10^{20}$ cm$^{-3}$ and 2.0 cm$^2$ V$^{-1}$s$^{-1}$. It was possible that both of Cl and V$_{O}$ contributed to the electric conductivity. On the other hand, the transmittance of the film was not fully improved even after the annealing in O$_2$ and the color was probably due to doped chlorine.

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References