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SnO_2 Coatings on Porous $LiAl_5O_8$ by Simple Thermal Evaporation Process

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Abstract

Thermal evaporation process has special practical advantages of being technologically simple and being able to carry out with a low cost, which could be applied especially in technologically-under-developing countries. Tin powder was filled in an alumina crucible by volumetric ratios of Sn to Air as 0.17. The porous $LiAl_5O_8$ prepared by the reaction bonded sintering was set above the tin powder by 5 mm. Temperatures at 700°C, 800°C, 900°C, 950°C and 1000°C were selected for the evaporation process of tin powder to coat on the porous $LiAl_5O_8$ substrate for 6 hours. The coating temperature of 950°C showed a high deposition rate. The SnO_2 did not cover all the surface of $LiAl_5O_8$. The SnO_2 deposited on $LiAl_5O_8$ looks like islands pattern. The electrical conductivity measurement showed the present $SnO_2/LiAl_5O_8$ material system had the electrical conductivity similar to that of the porous $LiAl_5O_8$. Deposited amount of SnO_2 was not large enough to affect the electrical conductivity of the system.

Keywords: Simple thermal evaporation, SnO_2, Poroua $LiAl_5O_8$, Electrical conductivity

1. Introduction

SnO_2 is a wide band gap energy semiconductor which used for gas sensor to detect combustible, toxic and pollutant gases (1-3). The reason of SnO_2 as a sensor is because of its high sensitivity, simple design and low cost. Several attempts have been made to improved sensitivity and selectivity of SnO_2 for smart gas sensors. Adoption of a porous substrate is one method to improve the sensitivity. Materials with a large surface area and a high porosity could adsorb a lot of gas. One of lithium/aluminium oxides, lithium penta-aluminate ($LiAl_5O_8$) is one of attractive candidates as a porous substrate. $LiAl_5O_8$ is a refractory ceramics and its well-sintered material has a good mechanical property. Also, it is light in weight. These properties are very important for applications. Furthermore, $LiAl_5O_8$ has a spinel crystal structure, in which Li+ ions can be substituted with other metallic cations, modifying local charge misfits. Resultantly, $LiAl_5O_8$ has much higher electrical conductivity than α-alumina (Al_2O_3). It is known that the spinel structure has in general good radiation resistance due to its flexible atomic structures. This will give us good prospects for application of $SnO_2/LiAl_5O_8$ sensors in nuclear environments.

When SnO_2 layers are used in gas sensors, some features can depend on many parameters of microstructures of deposited layers such as thickness, cluster size, roughness, etc. The materials properties depend on the preparation process. Nowadays, various techniques have been used to obtain SnO_2 thin films such as spray pyrolysis (4), DC magnetron reactive sputtering and RF sputtering (5), evaporation in reactive atmosphere and electron beam evaporation (6), sol gel (7), chemical vapor deposition (CVD) (8), laser methods and plasma oxidation (9). In general, sophisticated instrumentations are needed to control detailed microstructures of deposited layers, and well-trained-craftsmanship is needed to establish a high-grade quality-control. These conditions could be satisfied easily in industrialized countries, however, more simple and easy-to-control processes are desirable in under-industrializing countries.

A thermal evaporation process is simple and cheap to prepare SnO_2 thin film, which could be enjoyed and deployed especially in technologically-under-developing countries. Admitting that there will be some technological disadvantages in this simple process, such as being hard to control some important depositing parameters, the present study surveyed applicability of this simple thermal evaporation process for preparing SnO_2. To optimize deposition-conditions, two parameters were systematically studied, namely, a deposition duration and a deposition temperature.

2. Materials and Experiment

2.1 Deposition (Coating) time

Tin powder was filled in the alumina crucible by a volumetric ratio of Sn/Air of 0.17 v/v. The porous $LiAl_5O_8$ substrate, which was prepared by reaction bonded sintering at 1550°C was set 5 mm above tin powder, being suspended by platinum thin wire in the evaporation chamber. The volume of the evaporation chamber is about 36 cm^3 (3x3x4 cm^3). The annealing temperature was 950°C.

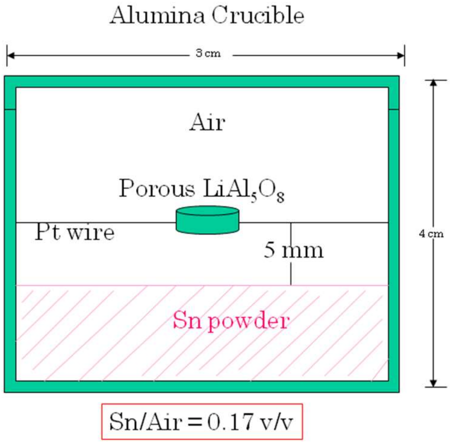

Figure 1 The schematic of experimental setup for thermal evaporation of Sn.

2.2 Deposition temperature

A deposition temperature is another important parameter to be optimized. The melting and the boiling temperatures of Tin (Sn) are 232°C and 2270°C, respectively. The melted Tin has a substantial vapor pressure above 600°C. Here, Temperature, 700°C, 800°C, 900°C, 950°C and 1000°C were selected used for evaporation process of tin powder to coat on porous $LiAl_5O_8$ substrate for 6 hours (Figure 1). The deposition time of 6 hours was selected from the first experiment described above.

Deposited SnO_2 was characterized by the scanning electron microscopy (SEM, Jeol model JSM-7610F) for its morphology and for estimation of semi-quantitative surface coverage degree. X-ray diffractometry (XRD, Shimadzu XRD 6000) was used for identifying a crystal structure of the deposited SnO_2 as well as for estimation of its deposited amount. The X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS 5100) was applied to study chemical bonding state of Tin in a $SnO_2/LiAl_5O_8$ system. The electrical conductivity of $SnO_2/LiAl_5O_8$ systems was measured as a function of temperature in the range of 25-400°C, with the specimen of 2 mm thick and 8 mm diameter as shown in Figure 2. The electrical conductivity was measured along its thickness.

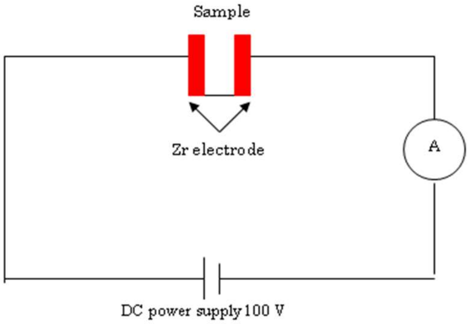

Figure 2 The schematic of electrical conductivity measurement for the $SnO_2/LiAl_5O_8$ specimens.

3. Results and Discussion

3.1 The effect of coating time

A deposition time is practically an important parameter. Its optimization will minimize a production cost and maximize a production efficiency. As the first step of the optimization of the present deposition process, an amount of SnO_2 deposted on its substrate was evaluated as a function of deposition time. Peak intensity of SnO_2 on the substrate in the conventional X-ray diffractometry (XRD) was used as a monitor for an amount of deposited SnO_2 on the $LiAl_5O_8$ substrate. The XRD results (Figure 3) shows SnO_2 (JCPDS card No.14-1445, 2θ 26.7(110)) and LiAl5O8 (JCPDS card No. 87-1278, 2θ 25.2(210), 27.8(211)).

Figure 3 and 4 shows the results, indicating that the deposited amount saturated after about 5-6 hours. Thus, the deposition time was fixed at 6 hours in the following experiments.

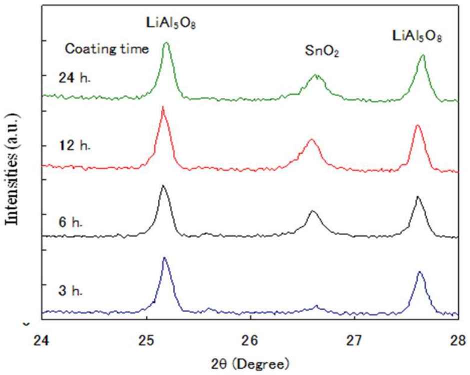

Figure 3 The XRD patterns specimens evaporated at 950°C for 3, 6, 12 and 24 h.

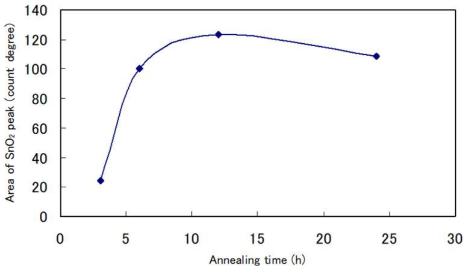

Figure 4 XRD peak intensities of SnO_2 plotted as a function of evaporating time.

As will be discussed in the followings, wettability of SnO_2 on the surface of $LiAl_5O_8$ is not good and it is speculated that the increase of the deposition time only resulted in the growth of diameters of granularly deposited SnO_2 and larger granular SnO_2 particles have strong tendency to drop off from its substrate. Improvement of the wettability will be an important technological challenge to overcome for application of the present material system. Doping of $LiAl_5O_8$ with some small amount of dopants will be one possible measure

3.2 The effect of coating temperature

The results of the X-ray diffractometry were shown in Figure 5 as a function of deposition temperature. The $LiAl_5O_8$ peak was a shift at deposition temperatures 800, 900 and 950°C. It is because SnO_2 can be deposited and substituted in structure of $LiAl_5O_8$ at these temperatures which can be made the $LiAl_5O_8$ peak was a shift. The diffraction peaks which could be identified as those from tin oxide (SnO_2) were identified only on samples prepared at 950°C, which happens to be near to the boiling temperature of tin in the atmospheric pressure. The sublimation temperature of the tin oxide (SnO_2) is reported to be about 1800-1900°C (10). The deposition processes of the SnO_2 in the present small chamber will not be simple, however, the most probable process could be a formation of tin vapor from a tin source and its deposition onto the substrate, then the reaction of tin with oxygen in the atmosphere. There is also a possibility that the tin vapor would react with oxygen along its evaporating path from the tin source to the depositing substrate. A rate of oxygen supply from the atmospheric environment to the tin will be an important parameter to control the actual deposition process. As will be shown and discussed below, the XPS results (Figure 7) showed that some tin atoms reacted with the $LiAl_5O_8$ substrate, suggesting that the tin atoms arrived at the substrate as a state of the tin (not a tin reacted with oxygen). Once tin dioxide (SnO_2) is formed, its melting point is above 1600°C and the present deposition temperatures were too low to allow the substantial reaction of SnO_2 with its substrate of $LiAl_5O_8$. There is some possibility that the thermally unstable Tin sub-oxide (SnO) may be formed along the evaporation path and it may react with its substrate.

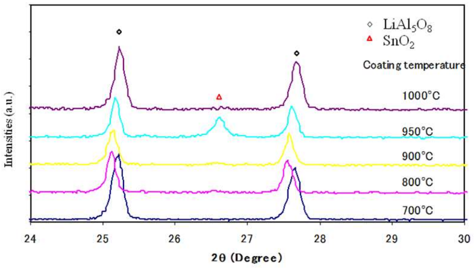

Figure 5 The XRD parttern of specimens coated at various temperature

Figure 6 shows the SEM photographs of SnO_2 coated at temperatures of 700°C, 800°C, 900°C, 950°C and 1000°C respectively. SnO_2 nano-wires and sub micro-meter size particles were found on the specimens coated at temperature 950°C (Figure 6 (d)) and their small amounts on specimens coated at the temperature of 900°C (Figure 6 (c)). Although results of the XPS showed that there exist tin atoms on the surface of the $LiAl_5O_8$ substrate at all the deposition temperatures, the SEM could not identify the existence of SnO_2 nano-wires nor submicron particles at the deposition temperatures other than 900°C and 950°C. The existence of the nano-wires are strongly suggesting that the tin atoms were deposited on the substrate as tin atoms and then again evaporate, where the re-evaporating tin will locally react with oxygen and form SnO_2. Here, the supplying rate of oxygen to the tin would be limited for some reasons. For the case of submicron particles, it is assumed that the deposited tin atoms would form a small melt droplet and then it would be oxidized. At 1000°C, the melt droplet will be unstable as the temperature exceeded the boiling temperature of tin. Below 900°C, the tin supplying rate (a tin evaporation rate from the tin feed) will not be high enough to form substantial amount of tin deposit on the substrate.

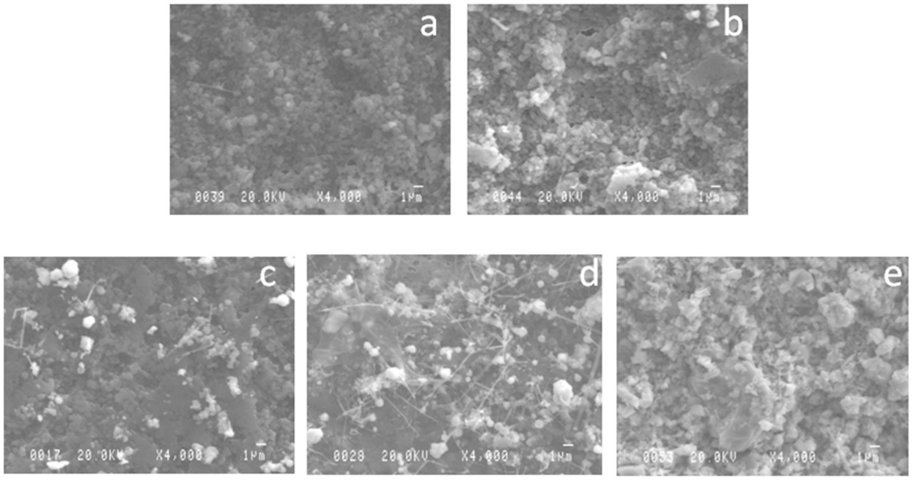

Figure 6 SEM photographs of coated specimen on porous $LiAl_5O_8$ with various temperature; (a) 700°C, (b) 800°C, (c) 900°C, (d) 950°C and (e) 1000°C

Figure 7 shows the XPS spectra from the Tin (Sn) in the $SnO_2/LiAl_5O_8$ systems. All the spectra clearly showed that there are two kinds of Tin in the system, one kind designated as the Sn in SnO_2 (a Sn $3d_{5/2}$) with a binding energy of about 498 eV, and the other kind designated as the Sn which is substituting Al cation sites in $LiAl_5O_8$ (b Sn $3d_{3/2}$) (11), with a binding energy of about 508 eV. The signal intensity of the both kinds of Sn is about the same, suggesting that chemical reaction of deposited Tin atoms with the substrate $LiAl_5O_8$ is substantial. The apparent shrinking of the lattice parameter of the $LiAl_5O_8$ with the increase of the deposition temperature except for the deposition at 700°C, may be explained by this substitution of 3+aluminium cations with 4+ tin cations, which will introduce cation vacancies in the lattice. The intensities of XPS were not consistent to XRD result. It is because the analysis point of XPS is very small point and films were not homogenous which look like islands pattern (Figure 8b). Therefore, it is difficult to select point for XPS analysis in accordance to XRD where the analysis point is larger.

A rough estimate of the deposited SnO_2 film thickness resulted in thinner than 10 nm, assuming that the film morphology is smooth and flat, covering uniformly all over the surface. This estimation of the thickness contradicts the fact that the SnO_2 diffraction peaks were clearly observed on the substrate. In the present conventional θ-2θ XRD, the X-ray diffraction peaks could be identified only if the film has a thickness larger than a few microns. The SEM photographs showed that a majority of deposited SnO_2 was in the nano-wires and the submicron particles. These results strongly indicate that the film morphology of the deposited SnO_2 films is not that of (a) in Figure 8 but that of (b) in Figure 8.

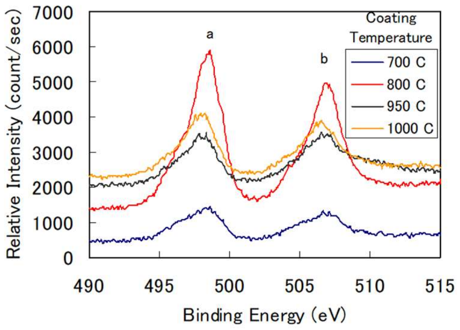

Figure 7 X-ray photoelectron (XPS) spectra of specimen coated at various temperature.

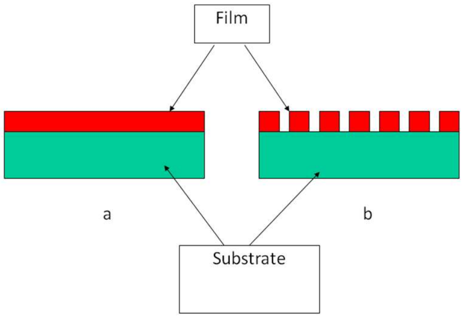

Figure 8 Schematic illustrator of deposited film on porous substrate from prediction (a) a thin film covers all the surface area of the substrate. (b) small particle distribution on the surface.

Figure 9 shows temperature dependence of the electrical conductivity of $LiAl_5O_8$ deposited with SnO_2. Only the specimen deposited with SnO_2 at 950ºC showed high electrical conductivity, more than one order higher than those deposited at other temperatures. In principle, $LiAl_5O_8$ is an electrical-insulator and SnO_2 is a semiconductor. The observed increase of the electrical conductivity and its large temperature dependence of the specimen deposited at 950ºC cannot be explained by the fact that the near-surface-region of the $LiAl_5O_8$ substrate was doped with the Sn as indicated by the XPS results. The results will be interpreted that the SnO_2 was penetrating into the porous $LiAl_5O_8$ and there were substantial electrical-conductive paths along the thickness of the substrate. The results of the electrical conductivity measurements also support that the deposition temperature of 950°C is the best for the present system.

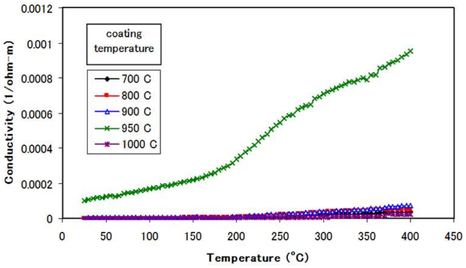

Figure 9 Temperature dependence of electrical conductivity of specimen coated at different temperature.

4. Conclusions

Tin oxide (SnO_2) is an optically transparent semiconductor and has many electrically attractive features. A system of SnO_2 deposited on some insulating materials, which should have some characteristics appropriate for their application, will reveal unexpected applications. In the present thermal evaporation system, an optimum coating rate of tin oxide was obtained at 950°C for about 6 hours. The characterization of the deposited SnO_2 indicated that desirable nano-structure was effectively formed on the porous $LiAl_5O_8$ substrate. The SnO_2 film on the porous $LiAl_5O_8$ substrate looks like islands pattern. Deposited amount of SnO_2 was not large enough to affect the electrical conductivity of the system.

Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

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