Electrodeposition is a powerful and interesting process that can be applied in numerous fields. Films and powders can be synthesized at a low temperature by electrodeposition because of the high energy density accumulated in solution near the electrode surface. The advantages of electrodeposition compared with other techniques include low process temperature, low cost for raw materials and equipment, capability of controlling composition and morphology by electrochemical parameters, and the ability to deposit films on a complex surface. Electrodeposition has already been commonly employed to prepare metallic coatings for more than one hundred years. In recent years, metal oxides synthesized by electrodeposition including zinc oxide,\textsuperscript{1,2} zirconium oxide,\textsuperscript{3} bismuth oxide,\textsuperscript{4} tungsten oxide,\textsuperscript{5} and metal oxide composites\textsuperscript{6} have been an active research area. In particular, through proper parameter control, deposited materials from nanocrystalline coatings to even epitaxial films\textsuperscript{7} with superior properties can also be achieved.

Tin oxide is one of the ceramic materials that is widely used because of its excellent properties for catalysis, gas sensor as anode materials of secondary lithium batteries, and as transparent conductive films for displays and solar cells. The interesting characteristics and related applications were dominated by several factors, such as morphology, grain size, crystallinity, and so on. For the electrodeposition of metal oxides, it is necessary for the hydroxyl ions or $O^-$ radicals to be present near the electrode surface. Previous research reported several oxygen sources, including hydrogen peroxide,\textsuperscript{2} nitric acid,\textsuperscript{1} and blown oxygen,\textsuperscript{8} which are the necessary components for electrodeposition of metal oxides. If nitric acid is chosen as the oxygen source, the half-reaction on the cathode electrode surface is expressed as follows\textsuperscript{9}

$$\text{NO}_3^- + H_2O + 2e^- \rightarrow \text{NO}_2^- + 2 \text{OH}^- \quad [1]$$

or

$$\text{NO}_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10 \text{OH}^- \quad [2]$$

The hydroxyl groups are formed on the electrode surface and contact with metal ions coming from the solution to synthesize metal hydroxide or metal oxide according to Reaction 3

$$M^{n+} + n\text{OH}^- \rightarrow M(\text{OH})_n \rightarrow MO_{n/2} + n/2\text{H}_2\text{O} \quad [3]$$

Because of low solubility, the metal hydroxide precipitates on the electrode surface rapidly. If the deposition temperature is higher than a critical temperature, metal hydroxide dehydrates and then metal oxide is synthesized. Because Sn is an amphoteric element,\textsuperscript{10} stannic or stannous ions react with hydroxyl groups to form $\text{SnO}_2^{2-}$ or $\text{Sn(OH)}_2^{2-}$ or other tin-based salts instead of metal oxide (or metal hydroxide). Therefore, the mechanism of electroplating tin oxide may be more complex than that mentioned above.

Although electrodeposition has been successfully employed for the preparation of coatings and powders of many metal oxides, to our knowledge, no electrodeposition process has been reported that is able to prepare the tin oxide films. The advantages of electrodeposition mentioned above, such as low cost, low temperature, and capability of obtaining nanocrystalline microstructures, also can be expected in electrodeposition tin oxide. Therefore, a novel process to deposit tin oxide by electrodeposition was conducted in this study. The structure characterization and phase identification were performed by X-ray diffraction (XRD), the bondings of the product in electrochemical reaction were determined by Fourier transform infrared (FTIR) spectroscopy, the morphology was observed by scanning electron microscopy (SEM), and the grain size was determined by transmission electron microscopy (TEM).

**Experimental**

The solutions for electrodeposition were composed of 20 mM tin dichloride (Riedel-de Haen, 99.8%), 100 mM sodium nitrate (99%), 75 mM nitric acid (J. T. Backer, A.C.S. reagent), and redistilled water. The mixed solutions were held at a bath temperature of 85°C for 3 h in order to obtain a stabilized solution. The working electrode was a copper disk (Alfa Aesar, 99.8%) of 1 cm diameter, which was cleaned with acetone and dilute hydrochloric acid solution. The electrochemical cell for deposition was a conventional three-electrode cell in which a tin metal plate (Aldrich, 99.9%) was used as the counter electrode with a separation from the working electrode by 2 cm. An Ag/AgCl electrode in a 3 M NaCl solution was used as the reference electrode. Films were deposited using a potentiotstat (EG&G, model 263A) with current densities ranging from 1 to 15 mA cm\textsuperscript{-2}. Duration of 10-200 min for electrodeposition has been chosen. The deposits were washed with water and then immersed in deionized water to leach the remaining chloride impurity. The specimens were dried at room temperature and some of them were heat-treated at 200 and 400°C, respectively, for 4 h. Samples were heat-treated in vacuum to inhibit the oxidation of the copper substrates and then were analyzed further in order to reveal the phase evolution and characteristics of the deposits.

Infrared analysis of the samples was performed on a Jasco FTIR 460 spectrometer. The deposited films were scraped off as powders from the substrate and mixed with potassium bromide powders as reference for FTIR analysis. Spectra were obtained at a resolution of 4 cm\textsuperscript{-1}. Phase of the films was characterized by XRD (Rigaku, model D/MAS III, V) with a monochromatic Cu Kα radiation (1.5405 Å). Surface morphology and structure of the coatings were analyzed by means of SEM (Philips XL-40FEG) and TEM (JEOL AEM 3010 microscopy), respectively. Grain size was calculated by the X-ray line broadening method using the Scherrer formula of $D$
In spectrum a, the adsorption peak at 593 cm$^{-1}$ is characterized as the vibration absorption of the Sn-O bond in SnO$_2$. Since the stretching adsorption of the O-H bond appears at 3363 cm$^{-1}$, the composition of the as-deposited film could be stannic oxide and stannic hydroxide. Because there is no Sn-OH bond adsorption peak located at 530 cm$^{-1}$ (labeled by an arrow), the O-H peak could be attributed to the adsorption of water molecules on tin oxide. According to the analysis, the as-deposited film is stannic oxide with adsorbed water molecules. The peak at 3169 cm$^{-1}$ was characterized as the adsorption of N-H bond in ammonium ion, because the electrochemical reaction described by Eq. 2 and the oxidation of stannous ion by nitric acid could be the source of ammonium ions. The number and position of N-H adsorption peaks can reflect the possibilities of hydrogen bonding within the crystal. A broad N-H adsorption peak in the range from 3100 to 3200 cm$^{-1}$ shows some degree of hydrogen bonding, which can be attributed to the adsorption of ammonium ions on tin oxide as described in a former report. Heat-treatment at 200°C for 4 h results in the partial desorption of adsorbed ammonium ions and water molecules. When the heat-treating temperature was 400°C, spectrum c shows an absence of N—H and O—H bonds, and SnO$_2$ was the only product formed from a process similar to a chemical reaction involving the interference of nitrogen gas.

The TEM micrograph and diffraction rings for electron diffraction from SnO$_2$ films as heat-treated at 400°C for 4 h in vacuum are shown in Fig. 3. The bright field image shows equiaxial and even spherical grains with a dimension between 4 and 7 nm. The ultrafine grains were observed in all specimens deposited at different current density. The result of grain size measurement from TEM observation is similar to that from X-ray line broadening method. It is interesting to find that for the electrodeposition of tin oxide, the grain size is much smaller than most of the other oxides prepared by different processes. Under the condition of ultrafine grain size, oxide coatings could still be observed as well-defined crystallites, and tetragonal structure of the SnO$_2$ also can be characterized by indexing the ring pattern. In the bright field image for the as-deposited sample, the shape of grains is similar to that shown in Fig. 3, but with rather different characteristics. An amorphous phase was obtained because of the presence of a hollow ring instead of a diffraction ring or a spot pattern. According to the shape and crystallinity of the as-deposited SnO$_2$, it is suggested that the SnO$_2$ might precipitate from a process similar to a chemical reaction involving the formation of SnO$_2$; meanwhile, the amorphous grains might be formed from the hydrolysis of stannic ions. The ultrafine particles.
can be attributed to a repeated nucleation process on the electrode surface. SnO$_2$ nuclei then aggregated into larger particles, and later stacked to form the SnO$_2$ coatings.

The morphologies of as-heat-treated SnO$_2$ films prepared at different current densities are shown in Fig. 4. Even for samples obtained from different current densities, the morphologies of the as-heat-treated and the as-deposited samples are almost the same, except for the formation of some cracks. The sample prepared at 1 mA cm$^{-2}$ is a smooth and transparent film observed by the naked eye and under lower SEM amplification, but under higher magnification of 20,000 times, the surface exhibits a bit of roughness. As the current density was higher than 5 mA cm$^{-2}$, fine grains aggregated and formed a porous surface. For deposition current density at 5, 10 and 15 mA cm$^{-2}$, larger nodules resulting from aggregation of fine particles were obtained with the average sizes of 60, 100, and 150 nm, respectively, as shown in Fig. 4b, c, and d. When the current density was higher than 15 mA cm$^{-2}$, the voltage was raised to higher than $-0.7$ V, the nitric acid ions near the electrode were consumed and then hydrogen gas formed. As a consequence, SnO$_2$ coatings with cracks then started to peel off the substrate because of the evolution of hydrogen gas.

A region of higher pH value was formed when hydroxyl groups were produced from nitric acid. As far as we know, in the absence of complex ions in aqueous solution, stannic ions tend to give a precipitate of hydrous tin(IV) oxide, which is easier to precipitate with increasing pH value.$^{10}$ Because of the phenomenon mentioned above, the region of higher pH value near electrode surface, which can contribute to the formation of hydroxyl groups, is the precipitation zone for tin oxide. When the current density was as low as 1 mA cm$^{-2}$, the rate of hydroxyl group generation was too slow to substantially promote pH value of the precipitation zone, and tin oxide precipitated at these positions very near the electrode surface. Therefore, a dense and smooth film gradually formed as shown in the Fig. 4a. Larger current densities resulted in formation of more hydroxyl groups on the electrode surface and pH value of the precipitation zone was higher. As a result of the rate of hydroxyl group generation and mass transport the regions suitable for hydroxide precipitation was wider than that for lower current density. Therefore precipitation of SnO$_2$ was easier and faster, which consumed more stannic ions near the electrode, and a gradient of stannic ions was thus formed. It is possible for SnO$_2$ to precipitate far from the electrode surface because of higher pH value and the presence of a stannic ion concentration gradient. Under such a situation, many protrusions of SnO$_2$ were formed on the electrode surface, and more hydroxyl groups were generated near them. The protrusions of SnO$_2$ were expected to contact the zone with more hydroxyl groups and stannic ions than that in the other areas. Therefore, most SnO$_2$ particles deposited on protrusions preferentially and then the SnO$_2$ film tended to grow toward the bulk solution from such places. Because of the above-mentioned behavior, morphologies turned from a smooth surface into a porous surface with increasing current density as shown in Fig. 4b, c, and d. Since tin is an amphoteric element, its chemical state is quite complex in a solution having varied pH value near the cathode during the electrodeposition process. The mechanism for the electrodeposition of tin oxide requires further study, and the work is under progress.

**Conclusion**

Nanostructured SnO$_2$ was prepared successfully on copper substrate by electrochemical deposition. The results of FTIR, XRD, TEM, and SEM are used to characterize the electrodeposition process and the resulting oxide films. The ultrafine grains, ranging between 4 and 7 nm, can be attributed to the repeated nucleation events of precipitation of SnO$_2$ on the electrode surface. At a low temperature of 85°C, the as-deposited films were synthesized with only a low degree of crystallinity, but it can be greatly promoted by heat-treatment at 400°C. Absorbed ammonium ions and water molecules can be burned out by heat-treatment at 400°C in a vacuum, and the tetragonal SnO$_2$ was the only product. Both dense and porous SnO$_2$ could be prepared by changing current density, and a porous surface can be prepared at the current density range of 5-15 mA cm$^{-2}$. When the current density was higher than 15 mA cm$^{-2}$, SnO$_2$ film started to peel off due to the evolution of hydrogen gas.

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