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Synthesis of tin and tin oxide nanoparticles using liquid phase plasma in an aqueous solution

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ABSTRACT

Liquid phase plasma method was applied to the synthesis of Sn nanoparticles. Tin chloride was used as the tin precursor. Dendrite-shaped particles were formed at the initial stage of the reaction, while spherical nanoparticles were generated at longer discharge time. When the discharge time was too long (longer than 50 min in this study), anisotropic SnO_2 nanoparticles were produced. With increasing dosage of Cetyltrimethylammonium bromide, used as the surfactant, the Sn particle size decreased, while the degree of dispersion of the particles increased. Higher electrical conductivity of the reactant solution resulted in the production of larger Sn nanoparticles. The solution pH decreased with increasing plasma discharge time until 50 min, after which pH slightly increased, co-occurring with the formation of SnO_2 nanoparticles.

1. Introduction

Metallic nanoparticles have been widely studied because they are of particular interest in many applications [1,2]. Among the wide variety of metal nanoparticles, methods for fabrication of tin nanoparticles have been frequently proposed in recent years [3–5]. Tin is predominantly considered as a solder material, which has long been used as a representative interconnection material in microelectronic applications [6–8]. In particular, the application of tin nanoparticles in the form of paste or ink materials is preferred for the interconnection in microelectronic applications [9,10]. Current techniques used to produce tin nanoparticles can be divided into chemical and physical methods. Chemical methods often involve toxic chemicals which may be dangerous for our environment. Preparation of ultrafine tin nanoparticles using physical methods, though it may be more environment-friendly, is usually more difficult. In particular, glow discharge in liquid phase is an environment-friendly method for the synthesis of metal nanoparticles. Liquid-phase plasma (LPP) can potentially fabricate metal nanoparticles rapidly without adding reducing agents because it provides a reaction field with highly excited energy states.

Recently, LPP method has attracted much attention, because it is a simple and practicable method and the size distribution, morphology, and composition of nanoparticles can be controlled easily [11–13]. Liquid phase plasma is defined as a discharge in aqueous solution, stabilized by the exchange of ions and electrons in liquid phase. This plasma generates a number of active species, e.g., hydrogen, oxygen, and hydroxyl radicals, in the solution. The reactants of the desired reaction are added into the solution and they react with the active species. By using the LPP method, metal nanoparticles can be generated via the reduction of metal ions through the reaction with hydrogen radicals, without the addition of any reducing agent. This method was found to be a very effective process for rapid synthesis of metal nanoparticles [13,14].

In this study, the LPP method was used to produce tin nanoparticles from a solution of tin chloride. A bipolar pulsed electrical discharge system was used to produce LPP. The effects of affecting factors, including the tin chloride concentration, surfactant concentration, and discharge duration, on the size and morphology of the produced particles were investigated. The features of nanocrystals were characterized using transmission electron microscopy (TEM).

2. Experimental

The LPP experimental device consists of four main parts: (1) an LPP reduction reactor with two tungsten electrodes, (2) a power supply system which can control the pulsed discharge parameters, (3) a reactant solution that is circulated for cooling, and (4) a spectroscopic analysis system for the detection of optical emission

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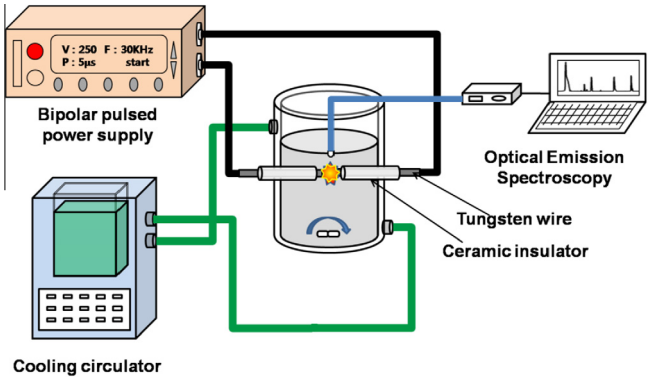

Fig. 1. Schematic of the experimental system with liquid-phase bipolar pulsed electrical discharge.

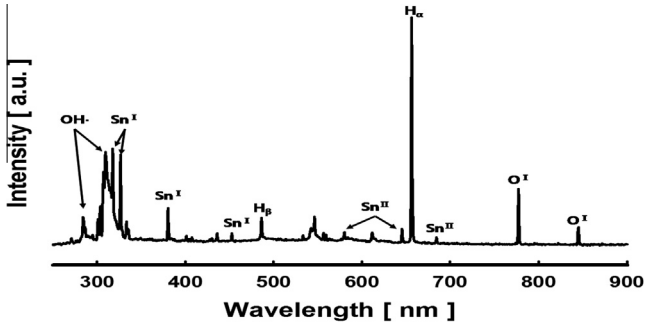

Fig. 2. Spatially and temporally integrated emission spectra for the pulsed electric discharge in $SnCl_2$ solution.

spectra. A schematic diagram of the experimental setup used in this study is shown in Fig. 1. Similar apparatus was used in our previous study to generate Ag nanoparticles dispersed in an aqueous solution using the LPP process [13]. Detailed information of the experimental setup can be found in that paper [13]. Pulsed electric discharge was generated by an electrode system in a double annular tube type reactor (ID 50 mm, OD 80 mm, height 150 mm). The applied voltage, pulse width, and frequency were 250 V, 5 μs, and 30 kHz, respectively.

The reactant solution was prepared by adding surfactant to an aqueous solution of a tin precursor. Tin chloride dehydrate ($SnCl_2 \cdot 2H_2O$, Junsei chemical Co. Ltd.) was used as the precursor. Cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, Daejung Chemicals & metals Co., Ltd.) was used as the surfactant to allow good dispersion of the tin nanoparticles generated in the reactant solution. All the chemicals used in this study were reagent-grade. Pure water (Daejung Chemicals & metals Co., Ltd.) was used throughout the study. The total volume of the reactant solution was 300 ml. The concentration of Tin chloride ($SnCl_2$) was 2–4 mM. The CTAB concentration was controlled within the range of 0–50% of the $SnCl_2$ concentration used.

The reactant solution prepared in the above-mentioned way was put in the double annular tube type reactor shown in Fig. 1. Liquid phase plasma reaction was induced by applying electric power to the electrode. To prevent steady increase in the temperature of the reactant solution due to the plasma and to maintain a constant reaction temperature (298 K), coolant (30% ethylene glycol, 268 K) was circulated through the outer channel of the reactor. The reactant solution was sampled at different plasma discharge time and analyzed using various instruments.

The emission spectrum of the plasma-discharged $SnCl_2$ solution was recorded by an optical emission spectrometer (AvaSpec-3648, Avantes). A field emission transmission electron microscope (FETEM, TECNAI-20, FEI) was used to observe the morphology, size, and the degree of dispersion of the Sn particles generated. The lattice and electron diffraction (ED) pattern of the Sn particle were observed using a high resolution FETEM (HR-FETEM, JEM-2100F, JEOL). The white slurry formed by a long plasma reaction was observed using a field emission scanning electron microscope (FESEM, JSM-7100F, JEOL) equipped with an energy dispersive X-ray (EDX) analyzer.

3. Results and discussion

3.1. Characterization of activated chemical species

Fig. 2 shows an optical emission spectrum obtained when LPP was created in the tin chloride solution. The emission peaks of Sn^{I} (318, 326, 380, and 452 nm) and Sn^{II} (580, 645, and 684 nm) corresponding to the energy levels of Sn, as well as the peaks of active chemicals, e.g., OH radical (285 and 309 nm), H_α (656 nm), H_β (486 nm), and O^{I} (777 and 845 nm), produced by the LPP, were observed [15]. This spectrum suggests that the tin precursor Sn^{2+} was reduced to Sn forming nanoparticles via the reaction with active chemicals.

3.2. Effects of surfactant

To investigate the effect of the surfactant dosage on the morphology and degree of dispersion of Sn particles produced, the experiments were repeated with different CTAB dosages. Fig. 3 shows the TEM images of the Sn particles produced by the LPP process with different molar ratios of CTAB: 0%, 10%, 30%, 50% (of the precursor concentration). The $SnCl_2$ concentration was 3 mM and the plasma discharge time was 50 min for every experiment.

When no CTAB was added, the particle size was 20–100 nm and some particles were aggregated. With increasing CTAB dosage, the particle size decreased and the degree of dispersion of the particles increased. When the CTAB molar ratio was 50%, the size of the particles was smaller than 15 nm, being nanoparticles dispersed very well.

A surfactant molecule is composed of a hydrophilic part with electrical charge, and a nonpolar hydrophobic part. When the cationic surfactant CTAB is used, the positive hydrophilic part of CTAB is oriented toward the surface of the negative tin particle surface, covering the tin nanoparticles effectively and repelling tin ions. Generally, addition of surfactant influences the nanoparticle generation process through the electrostatic interaction between the nanoparticle surface and the surfactant. Spherical nanoparticles are generated when particles are very small, whereas as a particle grows, specific shape may develop to minimize the total surface energy. In order for a surfactant to intervene in the particle growth, it has to combine with the particle surface. The connection between the particle surface and the surfactant takes place selectively for specific surface orientation. This effect of CTAB is believed to have led to generation of small nanoparticles shown in Fig. 3d.

3.3. Effects of discharge time

Fig. 4 shows the TEM images of the Sn particles generated from the LPP process with different discharge times. In every experiment, the $SnCl_2$ concentration of the reactant solution was 3 mM and the CTAB molar ratio was 50%. When the discharge time was 10 min, the Sn particles were dendrite-shaped, with their size of approximately 50 nm. The particle size decreased with increasing discharge time. When the plasma discharge time was 50 min, Sn particles were well dispersed spherical nanoparticles, with their size smaller than 15 nm.

Saito et al. [12] synthesized gold nanoparticles using the solution plasma method. They proposed the following mechanism for