



Synthesis and film deposition of Ni nanoparticles for base metal electrode applications

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ABSTRACT

This paper describes the preparation of Ni thin films for base metal electrode applications using Ni nanoparticles that were synthesized by thermal decomposition of a Ni–oleate complex under inert gas flow. The oleate molecules both retarded particle growth and prevented oxidation. The mean particle sizes of the cubic phase Ni nanoparticles synthesized at decomposition temperatures of 350, 380, and 400 °C were 5.1, 5.5, and 6.6 nm, respectively. The average activation energy for Ni nanoparticle formation was $157.51 \pm 13 \text{ kJ mol}^{-1}$, revealing a single kinetic mechanism. After formulation of a moveable paste, the Ni nanoparticles were well-dispersed on a silicon wafer using a spin coater. The deposited Ni films were further investigated for sintering behavior. Based on the cross-sectional images, the thickness of the as-deposited Ni film was 2.5 μm , while the film sintered at 800 °C was 1- μm thick. The sintered Ni films had a high continuity, without any cracks or voids. The bulk resistivity of the Ni film sintered at 800 °C was $1.8 \times 10^{-5} \Omega \text{ cm}$.

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1. Introduction

Nickel (Ni) nanoparticles have been used in a wide variety of applications, such as conducting inks, multi-layered ceramic capacitors (MLCCs), microelectronics, thick-film electrode material in microelectronic passive components, and solar-cell applications, because of their unique physical and chemical properties [1–6]. The physical and chemical properties of Ni nanoparticles are directly controlled by particle size and shape, inter-particle distance, structural phase, and the properties of the supporting materials.

Liquid phase syntheses, including thermal decomposition methods, have been widely used to prepare Ni nanoparticles due to the advantages of controlled particle size, cost savings, mass production, and so on [1,2,6–10]. Ni nanoparticles with various morphologies (i.e., spherical, petal-like, and nanowires) and controlled particle size were obtained using these synthesis processes [1,2,7]. For example, highly monodispersed Ni nanoparticles with the sizes ranging from 2 to 7 nm were synthesized using a hot surfactant solution [1]. Furthermore, these processes can be performed using either hot surfactant solutions (more than 200 °C) or toxic reducing agents (e.g., hydrazine, *N,N*-dimethylformide, etc.). However, these methods cannot be applied in industry because the chemicals that are required for the preparation of Ni nanoparticles are toxic

and expensive. Ni nanoparticles that are synthesized for industrial applications must be produced in a simple process, using relatively non-toxic precursors that are not oxidized when exposed to air. In addition, for film deposition, the Ni nanoparticles must readily disperse in organic materials (e.g., polymers, binders, and so on), so that the deposited film is continuous with no voids or cracks [11,12].

To date, ultra-fine Ni particles, ranging in size from 0.1 to 1 μm , have been widely used in thin-film electrodes, such as MLCCs [12]. Synthesis of the thin-film internal electrodes of MLCCs requires Ni nanoparticles that are below 1 μm . However, if the particles are less than 100 nm, the deposited layer shrinks excessively after firing, resulting in porous thin films with high bulk resistivity [11]. The morphology, thickness, porosity, and densification of sintered Ni films depend on how well the Ni particles are dispersed in the organic binder. An unstable paste formulation can result in irregular shrinkage during decomposition of the organic binder. Im et al. reported that the dispersity of Ni paste was improved by use of a binary-sized Ni particle mixture [12]. Compared with mono-sized Ni particles, the Ni film resulting from binary-sized particles exhibited reduced surface roughness. However, because of high solid-loading, pastes containing binary-sized Ni particles are more viscous. As a result, the dispersibility of the Ni paste is reduced, and surface roughness is increased. Thus, for a Ni film with full densification, the Ni particles should be well-dispersed in a low-viscosity medium. Generally speaking, because nanoparticles have large surface areas, they tend to agglomerate to decrease surface energy, resulting in the formation of porous Ni films. Conversely, if

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Ni nanoparticles with minimal agglomeration are well-dispersed in an organic binder, a Ni film with full densification may be obtained.

The purpose of the present study was to prepare a Ni thin film using Ni nanoparticles that were synthesized by thermal decomposition of a Ni–oleate complex under an inert gas atmosphere. Previous reports indicate that oleate both retards particle growth and inhibits oxidation [13,14]. Using thermal decomposition of Ni–oleate, Ni nanoparticles with less agglomeration were produced. The effects of decomposition temperature on particle size, morphology, shape, and crystal structure were systematically examined. The calculation of activation energy of Ni nanoparticle formation was carried out using the isoconversion methods of Ozawa and Kissinger–Akahira–Sunose (KAS) [15,16]. Because the Ni nanoparticles were well-dispersed in the organic binder, they were widely spread on a flat substrate, with high continuity, using a spin-coater. After deposition, the sintering behavior and bulk resistivity of as-deposited Ni films were also analyzed as a function of sintering temperature. The synthesis and film deposition processes described in this article can be directly applied to the preparation of MLCCs with high continuity and smooth surfaces.

2. Materials and methods

2.1. Materials

The synthesis of the Ni nanoparticles was carried out using commercially available reagents. Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99+%, Kanto Chemicals, Japan) was selected as the Ni precursor. Sodium oleate ($\text{C}_{18}\text{H}_{33}\text{NaO}_2$, 95+%, Wako Chemicals, Japan) was used to retard particle growth and prevent particle oxidation during the thermal decomposition reaction. Absolute ethanol (99.9%, Kanto Chemicals, Japan) and hexane (96%, Wako Chemicals, Japan) were used as solvents. All chemicals were used as purchased without any further purification.

2.2. Preparation of Ni–oleate complex

The Ni–oleate complex was prepared by a ligand exchange reaction between nickel nitrate and sodium oleate. Nickel nitrate (10 mmol) and sodium oleate (30 mmol) were dissolved in a solvent mixture composed of 50 mL de-ionized (DI)-water, 50 mL ethanol, and 50 mL *n*-hexane. All chemicals were mixed with vigorous stirring, using a magnetic stir bar, at 20 °C and refluxed at 70 °C for 3 h. When the reaction was complete, the upper organic layer containing the Ni–oleate complex was washed three times with DI-water in a separatory funnel. After washing, the Ni–oleate complex was fully dried under a vacuum.

2.3. Synthesis and film deposition of Ni nanoparticles

The dried Ni–oleate complex was transferred to a glass tube reactor and decomposed under nitrogen (N_2) flow of 0.5 L min^{-1} at a heating rate of $15^\circ\text{C min}^{-1}$. To clarify the effect of decomposition temperature on particle size, the Ni–oleate complex was thermally decomposed at different temperatures. During the decomposition reaction, the Ni–oleate complex changed color from green to dark-brown, and finally a dark colored material was obtained, indicating the formation of Ni nanoparticles. The as-synthesized Ni nanoparticles were washed by centrifugation with the addition of ethanol and hexane in a volume ratio of 5:1 (ethanol/hexane). Finally the black product was dried at 25 °C under a N_2 atmosphere. Fig. 1 shows a schematic diagram of the synthesis of Ni nanoparticles using thermal decomposition.

A Ni paste was formulated by mixing the dried Ni nanopowders mixed with ethyl cellulous as a vehicle and α -terpineol as a solvent in a constant ratio of 30:35:35, respectively. The Ni paste was

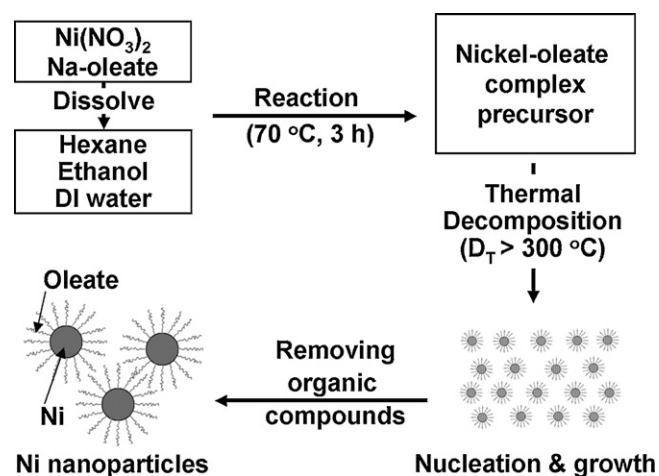


Fig. 1. Schematic diagram of the synthesis of Ni nanoparticles using thermal decomposition.

milled several times using a hand mill, and then was deposited on a silicon wafer using a spin coater (1H-D7, Mikasa Co. Inc., Tokyo, Japan). 100 μL of paste was spin coated to the silicon wafer substrate (1 cm \times 1 cm) with a constant spinning speed (1500 rpm) for 30 s. To investigate the dependence of the microstructure on sintering temperature, the deposited Ni thin films were sintered up to 800 °C at a heating rate of $10^\circ\text{C min}^{-1}$ under forming gas (with 5 vol.% H_2) atmosphere.

2.4. Characterization

The morphology and particle size of the as-synthesized Ni nanoparticles were observed using field emission scanning electron microscopy (FE-SEM, S-5000, Hitachi, Japan, operated at 20 kV) and field emission transmission electronic microscopy (FE-TEM, JEM-3000F, JEOL, Japan, operated at 300 kV). The microstructure and thickness of the Ni films were analyzed by SEM (S-3100, Hitachi, Japan, operated at 20 kV). The mean diameter and standard deviation were calculated from measured particle size based on FE-SEM and FE-TEM images of approximately 200 randomly chosen particles. The crystalline phase of the Ni nanoparticles was characterized using wide-angle X-ray diffraction (XRD, RINT 2200 V, Rigaku Denki, Tokyo, Japan) with nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5408 \text{ \AA}$) at 40 kV and 30 mA. Thermal gravimetric analysis (TGA, 6200, Seiko Instruments Inc., Japan) was performed. During the TGA measurements, approximately 10 mg of sample was placed in a platinum crucible and was heated over the temperature range of 50–600 °C under N_2 gas flow (0.2 L min^{-1}), at a heating rate of $10^\circ\text{C min}^{-1}$. The area-specific resistances of the as-deposited and sintered samples were measured using a four-probe system (Loresta GP Model MCP-T600, Mitsubishi Chemical Co., Japan).

3. Results and discussion

3.1. Thermo-chemical behavior of the Ni–oleate complex

To determine the formation temperature of Ni nanoparticles, the Ni–oleate complex was thermally characterized. Fig. 2 shows the thermo-chemical behavior of the Ni–oleate complex under a N_2 atmosphere based on results of TGA; differential thermal gravimetry (DTG) of the complex is also plotted. The total weight loss was 85% in the TGA plot, which was attributed to two distinct processes. Almost all of the weight loss occurred between 300 and 400 °C, indicating formation of Ni nanoparticles. Weight loss of only 7% was observed between 400 and 600 °C, indicating that weight loss may

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