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Multi-component co-condensation model of Ti-based boride/silicide nanoparticle growth in induction thermal plasmas

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Abstract

Numerical analysis is conducted for the titanium-based boride and silicide nanoparticle synthesis using an induction thermal plasma including the material evaporation process and the nanoparticle growth process with nucleation and co-condensation. Both systems present the nano-scaled particle size distributions. Ti–B system shows the smaller particle diameter, sharper distribution, larger particle number density, and wider range of the composition than Ti–Si system. Ti–Si system provides a narrower range of the silicon content due to the simultaneous co-condensation of titanium and silicon. Finally the correlation between the particle size and the nonmetal content of the synthesized nanoparticles is presented on a chart.

Keywords: Plasma processing and deposition; Nucleation; Boride; Silicide

1. Introduction

Induction thermal plasmas (ITPs) are well-known to have distinctive advantages such as high enthalpy, high chemical reactivity, variable properties, large plasma volume, and long residence/reaction time. Additionally, ITPs are inherently clean because they can be produced without internal electrodes [1–3]. ITPs have, therefore, been utilized for material and environmental processes such as nanoparticle synthesis, reactive plasma spraying, surface treatment, waste treatment, and decomposition of harmful substances [4–6]. Particularly, mass-production of metallic and ceramic nanoparticles with high purity using ITPs has been intensively expected, since it can be effectively achieved by high enthalpy and high quenching rate of the ITPs [7–10].

Titanium-based ceramics, especially the diboride and the disilicide, provide attractive properties and characteristics. Titanium-diboride TiB_2 displays high strength, durability, melting point, hardness, and wear resistance [11]. Thus, it has been applied as crucibles, cutting tools, impact-resistant armor, and wear-resistant coatings. It is also expected to be used as a cathode in the electrochemical reduction of alumina to aluminum metal. Titanium-disilicide provides high electrical conductivity and heat/oxidation resistance. Nanoparticles of the compounds are, therefore, expected to be applied for semiconductor technology as electromagnetic shielding, solar control windows, VLSI electrodes, and so on.

The synthesis of diboride/disilicide nanoparticles is, however, a difficult manufacturing process, and the production efficiency is still low compared with the cost. For the breakthrough of the problems, ITPs are considered to be intensively useful. If the manufacturing process is well-understood and controlled precisely, mass-production of diboride/disilicide nanoparticles will be easily achieved using ITPs under atmospheric pressure with low costs. The process of the synthesis is, however, a complicated phenomenon with many controlled parameters, and it includes a co-condensation process with large or small vapor pressure differences of prepared species. Although only a few studies and researches have been conducted concerning the synthesis of boride/silicide nanoparticles using ITPs up to now [12–14], the growth mechanisms of boride/silicide nanoparticles in ITPs are still poorly understood. Therefore, detailed investigation into the growth mechanisms of boride/silicide nanoparticles in ITPs is required for the precise control of the particle size distributions and stoichiometric compositions through the process.

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In the present study, numerical analysis is conducted for the titanium-based boride/silicide nanoparticle synthesis using an induction thermal plasma including the material evaporation process and the nanoparticle growth process with nucleation and co-condensation. The profile of the ITP is first determined by the electromagnetic fluid dynamics approach with consideration of chemical non-equilibrium of the plasma species for more accuracy. The precursor particle trajectory and temperature history are examined by Lagrangian approach taking into account the rarefied gas effects.

The nanoparticles of titanium-based borides and silicides are formed in the severe processes in which multi-component vapors co-condense and convert into nanoparticles in a very short period. Additionally, the growth mechanisms of both kinds of nanoparticles are considered to be different due to the differences of the vapor pressure ratios (B/Ti: 10^{-2}, Si/Ti: 10^{0}–10^{+1}). Therefore, a multi-component co-condensation model with higher spatial resolutions is proposed and applied individually to Ti–B system and Ti–Si system for clarification of the growth mechanisms of titanium-based boride/silicide nanoparticles. The validity of the present model is testified by comparison between the numerical results and the experimental results. Finally the correlation between the particle size and the nonmetal content of the synthesized nanoparticles is presented on a chart.

2. Numerical models

Fig. 1 shows a schematic illustration of nanoparticle synthesis systems consisting of a plasma torch and a reaction chamber [14]. A summary of the geometry and operating conditions is given in Table 1. The coil consists of three turns and applies the actual power 5.0 kW and the induction frequency 4.0 MHz to the plasma. Argon gas is injected as the carrier gas (1 Sl min^{-1}), the plasma supporting gas (13 Sl min^{-1}), and the sheath gas (20 Sl min^{-1}). Mixed powders of titanium and boron or silicon are supplied (0.1 g min^{-1}) as the raw materials for titanium-borides or titanium-silicides with the carrier gas from the central nozzle. After the powders are vaporized by the high enthalpy of the ITP, the vapors are transported with the plasma flow to the reaction chamber and become supersaturated due to the rapid temperature decrease there, which leads to homogeneous nucleation. Subsequently, the vapors co-condense on the nuclei. Nanoparticles of titanium-based borides or silicides are consequently synthesized from the gas phase. The titanium content of the feed powder is chosen to be 33.3 at.% to obtain the stoichiometric composition of TiB_2 and $TiSi_2$.

Table 1
Geometry and operating conditions of nanoparticle synthesis systems

Outer radius of inner slot (r_1):	6.5 mm
Outer radius of outer slot (r_2):	21.0 mm
Inner radius of injection tube (r_3):	1.0 mm
Inner radius of torch (r_4):	22.5 mm
Inner radius of chamber (r_5):	100.0 mm
Outer radius of injection tube (R_t):	4.5 mm
Radius of coils (R_C):	32.0 mm
Distance to frontal end of coil (L_1):	19.0 mm
Insertion length of probe (L_2):	45.0 mm
Distance to rear end of coil (L_3):	65.0 mm
Torch length (L_4):	190.0 mm
Distance to end of chamber (L_5):	380.0 mm
Torch power:	5.0 kW
Work frequency:	4.0 MHz
Coil turn number:	3
Pressure:	101.3 kPa
Wall thickness (δ_W):	1.5 mm
Flow rate of career gas (Q_1):	1.0 Sl min^{-1}
Flow rate of plasma gas (Q_2):	3.0 Sl min^{-1}
Flow rate of plasma gas (Q_3):	10.0 Sl min^{-1}
Flow rate of sheath gas (Q_4):	20.0 Sl min^{-1}
Powder feed rate:	0.1 g min^{-1}
Ti content of feed powders:	33.3 at.%

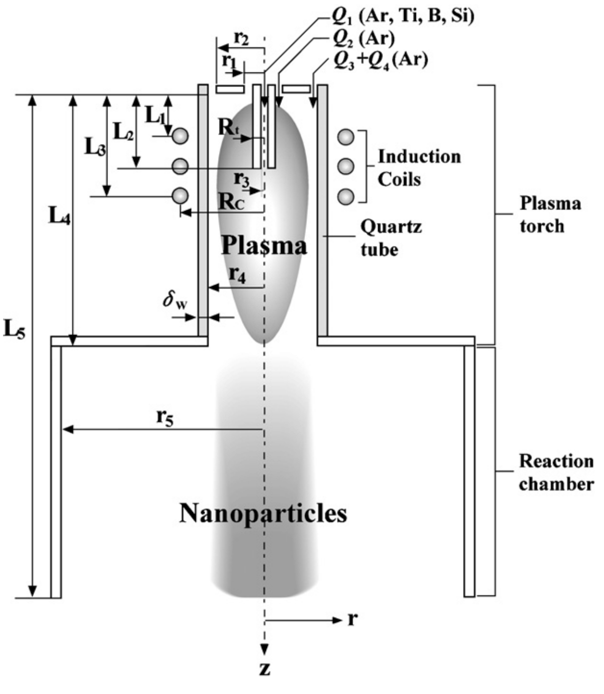

Fig. 1. Schematic illustration of nanoparticle synthesis systems.

2.1. ITP flow modeling

2.1.1. Assumptions

The computation is based on the following assumptions to derive the governing equations [14]: (a) steady-state laminar flow; (b) axial symmetry; (c) optically thin; (d) negligible viscous dissipation in energy equation; (e) negligible displacement current in comparison with conductive current; (f) negligible flow-induced electric field; (g) identical temperature of heavy particles and electrons; (h) negligible effects of metals and nonmetals on thermofluid fields or properties of a plasma flow.

2.1.2. Thermofluid fields and electromagnetic (EM) fields

The fields of flow, temperature and concentration in the induction thermal plasma flow are determined by solving the two-dimensional continuity, momentum, energy and species conservation equations coupled with the Maxwell's equations [14]. The non-equilibrium effects by the ionization and recombination were taken into account. The Electromagnetic (EM) fields are analyzed