Formation mechanism of silicide nanoparticles by induction thermal plasmas

Takayuki Watanabe*, Hideaki Okumiya

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Received 17 December 2003; revised 1 March 2004; accepted 3 March 2004
Available online 11 September 2004

Abstract

The condensation mechanism of metal mixture in thermal plasmas was investigated experimentally and numerically to prepare nanoparticles of silicon base intermetallic compounds. Silicon powder premixed with metal powder (Mo, Ti, Co, Fe, Cr, or Mn) was introduced into the plasma. The nanoparticles were prepared on condition that metal vapor was quickly quenched by the water-cooled copper coil. The nucleation rate expression was used for the estimation of critical saturation ratio. The nucleation temperature of the metal almost corresponds to the melting temperature, while silicon has wide liquid range between the nucleation and melting temperature, resulting in better preparation of silicide. For Mo–Si system, nucleation position of Mo is different from that of Si. Therefore, quenching position has strong effect on the particle composition of molybdenum silicide nanoparticles.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Thermal plasma; Nanoparticle; Silicide; Homogenous nucleation; Numerical analysis

1. Introduction

Induction thermal plasmas have been used for production of high-quality and high-performance materials, such as synthesis of nanoparticles, deposition of thin films, plasma spraying and treatments of powders. Induction thermal plasmas have been also applied for treatment of harmful waste materials and recovery of useful material from wastes [1,2]. These attractive material processes with induction thermal plasmas result from attractive advantages; these advantages include high enthalpy to enhance reaction kinetics, high chemical reactivity, large volume with low velocity, oxidation and reduction atmospheres in accordance with required chemical reactions, and rapid quenching (10⁶ K/s) to produce chemical non-equilibrium materials. These advantages increase the advances and demands in plasma chemistry and plasma processing, such as preparation of various kinds of nanoparticles in metallic and ceramic systems.

Silicide nanoparticles have high-electric conductivity, therefore these nanoparticles would be applied for the electromagnetic shielding, and solar control windows with interaction with IR and UV light. Preparation of silicide nanoparticles by induction thermal plasmas is the primary purpose of this paper.

Another purpose is to investigate the condensation mechanism of metal mixture vapor in thermal plasmas. Investigation of physical and chemical processes in thermal plasma processing is indispensable for production of nanoparticles. Co-condensation processes of metal vapors were investigated for Nb–Al and Nb–Si systems [3], Nb–Si and V–Si systems [4]. Vaporization processes for Ti–Si, V–Si and Mo–Si systems were also investigated [5]. For nanoparticle preparation with stoichiometric composition, the vaporization and condensation rates of the constituent metals should be controlled in the case of large difference in the vapor pressure.

2. Experimental procedures

The experimental set-ups consist of a plasma torch, a reaction chamber and a power supply of 4 MHz at 20 kW.
The plasma torch, 48 mm i.d., 127 mm length, consists of a water-cooled quartz tube and a working induction coil with 3 turn. The reaction chamber was set below the torch [6].

Si powder premixed with metal powder (Mo, Ti, Co, Fe, Cr, or Mn) was introduced into the plasma at the powder feed rate of 0.1 g/min. Feed powders used in this study are Si (10–25 μm, average: 15.7 μm), Mo (2–4 μm, average: 3 μm), Ti (1–25 μm, average: 9.1 μm), Co (1–25 μm, average: 5 μm), Fe (1–13 μm, average: 6.6 μm), Cr (0.7–25 μm, average: 9.6 μm), and Mn (0.6–25 μm, average: 10.5 μm). All powders have a purity of 99.9% and were supplied by High Purity Chemicals, Japan.

In the thermal plasma, the feed powders were evaporated immediately and nanoparticles were prepared through the cooling process. The nanoparticles were collected on condition that metal vapor was quickly quenched by the water-cooled coil.

The structures of the prepared nanoparticles were determined by X-ray diffractometry (XRD). XRD was carried out on an MXP3TA (Mac Science). The size distribution of the particles was measured from the photographs of transmission electron microscopy (TEM) for about 1000 particles. TEM observations were performed on JEM-2010 (JEOL) operated at an accelerating voltage of 200 kV.

3. Experimental results

3.1. Ti–Si system

First, the experimental result for Ti–Si system having small vapor pressure difference is presented. The vapor pressure ratio of Ti to Si is 0.9 at the melting point of Ti. The TEM photograph for Ti–Si system is shown in Fig. 1. The nanoparticles were prepared at the Ti content in the feed powders of 33% by the Ar plasma. The size distribution shown in Fig. 2 presents that the average particle diameter is 16.7 nm with the geometrical standard distribution of 1.39.

The XRD spectrum charts of the prepared nanoparticles for Ti–Si system are demonstrated in Fig. 3 with different Ti contents in the feed powders. TiSi2 and Ti5Si3 were identified as the silicides from XRD spectrum peak. Unreacted Ti and Si were also identified. The XRD results indicate that Ti5Si3 can be prepared more easily than TiSi2, because Ti5Si3 has large composition range as well as large solid solution range of 3%, while TiSi2 has small composition range. Fig. 4 shows the relation between the relative intensity XRD spectrum of Ti5Si3 and the initial composition at different quenching positions. Relative XRD intensity was defined as the ratio of Ti5Si3 first peak to the identified all first peaks (TiSi2, Ti5Si3, Ti, Si). Larger amount of Ti5Si3 particles was prepared at larger Ti content in the feed powders. The quenching condition has little effect on the prepared nanoparticle composition expect nanoparticle collected at the lower quenching; the nanoparticle composition at the lower quenching includes scattered composition, resulting from the instability of the plasma flame. Experimental results for Cr–Si, Fe–Si, Co–Si, Mn–Si systems providing the little effect of the initial composition of the injected particles on the prepared nanoparticle composition are attributed to the small difference between the nucleation temperatures of metal and Si as discussed later.
3.2. Mo–Si systems

The experimental result for Mo–Si system having large difference in vapor pressure is presented; the vapor pressure ratio of Mo to Si is $10^{-3}$ at the melting point of Mo. The XRD spectrum charts of the prepared nanoparticles for Mo–Si system with the Ar plasma are demonstrated in Fig. 5 with different Mo contents in the feed powders. MoSi$_2$ and Mo$_5$Si$_3$ with unreacted Mo and Si were identified from XRD spectrum peak. Fig. 6 shows the relation between the relative intensity XRD spectrum of MoSi$_2$ and the initial composition at different quenching positions. Relative XRD intensity was defined as the ratio of MoSi$_2$ first peak to the identified all first peaks (MoSi$_2$, Mo$_5$Si$_3$, Mo, Si). Preparation of MoSi$_2$ was most successful at the Mo 33% in the feed powders. The successful preparation of MoSi$_2$ results from the large composition range of MoSi$_2$. The quenching condition has strong effect on the prepared silicide composition for Mo–Si system, because of the large

![Fig. 3. XRD spectrum charts of nanoparticles for Ti–Si system; Ti content in the feed powders: (a) 33 at.%, (b) 50 at.%, and (c) 66 at.; powder feed rate: 0.1 g/min; upper quenching.](image)

![Fig. 4. Effect of quenching position on nanoparticles composition for Ti–Si system.](image)
difference between the nucleation temperatures of Mo and Si as discussed later.

4. Numerical simulation

Investigation of nanoparticle formation mechanism requires three kinds of numerical simulations: First, numerical analysis of plasma temperature and velocity fields; Second, numerical analysis of evaporation process of the injected powders in the plasmas; Third, numerical analysis of the nucleation process of the evaporated species.

4.1. Numerical analysis of plasma temperature and velocity

The fields of velocity and temperature in induction plasmas are important for investigation of nanoparticle preparation. Two-dimensional continuity, momentum and energy conservation equations with Maxwell’s electromagnetic equation were solved to calculate plasma velocity and temperature field. The calculations are based on the following assumptions: (a) steady-state laminar flow; (b) axial symmetry; (c) optically thin; (d) negligible viscous dissipation; (e) negligible displacement current.

Fig. 5. XRD spectrum charts of nanoparticles for Mo–Si system; Mo content in the feed powders: (a) 33 at.%, (b) 50 at.%, and (c) 66 at.%; powder feed rate: 0.1 g/min; upper quenching.

Fig. 6. Effect of quenching position on nanoparticles composition for Mo–Si system.
and flow-induced electric field; (f) local thermodynamic equilibrium for the ionization. The validity of these assumptions was discussed previously [1,7].

Continuity:
\[ \nabla \cdot (\rho u) = 0 \]  
where \( u \) is the velocity and \( \rho \) the density.

Momentum:
\[ \rho u \cdot \nabla u = -\nabla p + \nabla \cdot \tau + J \times B \]  
where \( p \) is the pressure and \( \tau \) the viscous stress tensor. The last term in the right-hand side is due to the Lorentz force.

Energy:
\[ \rho u \cdot \nabla h = \nabla \cdot \left( \frac{k}{C_p} \nabla h \right) - Q_r + J \cdot E \]  
where \( C_p \) is the specific heat at constant pressure, \( h \) the enthalpy, \( k \) the thermal conductivity, and \( Q_r \) the radiation loss per unit volume. The last term is due to the Joule heating. In these equations, the magnetic flux density \( B \), the electric field intensity \( E \), and the conduction current \( J \) were obtained from Maxwell’s equation.

The electromagnetic fields in this study were analyzed on the basis of the two-dimensional modeling approach with the electric field intensity as the fundamental variable [8]. Maxwell’s equations are expressed in terms of the electric field intensity as follows:
\[ \nabla^2 E - \frac{\xi}{\sigma_e} \frac{\partial E}{\partial t} = 0 \]  
where \( \xi \) is the magnetic permeability and \( \sigma_e \) the electrical conductivity. A sub-domain inside the plasma torch was used for the calculations of the electromagnetic fields.

The governing conservation equations were solved using SIMPLEC algorithm [9], which is a revision of SIMPLER (Semi-Implicit Method for Pressure Linked Equation Revised) algorithm [10]. The governing equations and the electric field intensity equation were discretized into finite difference form using the control-volume technique. The boundary conditions were the same as the previous studies [1,7].

The calculated plasma temperature distribution is shown in Fig. 7. The temperature field demonstrates that the high temperature region over 10,000 K is generated at the coil region. The highest temperature exists at off-axis position because of the skin effect of the electric field. The carrier gas from the injection tube is heated up rapidly. Therefore, melting and evaporation of the feed powders can be achieved easily.

4.2. Particle trajectory and temperature history with temperature jump model

Numerical simulation of the evaporation process of the injected feed powder in induction plasmas is the next task in this paper. Numerical simulation of the injected powder behavior is described in Section 4.2 for low Knudsen number region corresponding to the initial stage of the evaporation process for the injected powder having large diameter, and in Section 4.3 for high Knudsen number region corresponding to the last stage with small diameter of the injected powders.

The energy transfer regarded as the important interaction between plasmas and the feed powders was analyzed, because the prepared nanoparticle characteristics are significantly related to the feed powder behavior. The temperature history considering the melting and the evaporation of the feed powders can be estimated by an energy balance between the plasma and the powders. The powders were assumed to be injected axially from the injection tube with carrier gas into the plasma.

Temperature jump model and free molecular model were applied to the heat transfer estimation corresponding to the Knudsen number, \( Kn \), defined by Eq. (5).
\[ Kn = \frac{\lambda}{D} \]  
where \( D \) is the powder diameter and \( \lambda \) the mean free path of the molecules. For \( 10^{-2} < Kn < 0.1 \), a temperature jump boundary conditions have to be employed in conjunction with the continuum equations. The heat transfer equation for
a particle was used with a temperature jump model [11].

\[
Nu = (2 + 0.6Re^{1/2}Pr^{1/3}) \left( \frac{\rho_{\text{Ar}} u_w}{\rho_{\text{Ar}} \mu_w} \right)^{0.6} \left( \frac{C_{\text{Pr}}}{C_{\text{Pr}}^w} \right)^{0.38} \times H^{-1}
\]

(6)

\[
H = 1 + \left( \frac{2 - \alpha}{\alpha} \right) \left( \frac{\gamma}{1 + \gamma} \right)^4 \frac{Pr_m}{Pr_w} \times Kn
\]

where \( Nu \) is the Nusselt number, \( Pr \) the Prandtl number, \( Re \) the Reynolds number, \( \alpha \) the thermal accommodation coefficient, \( \gamma \) the specific heat ratio, and \( \mu \) the viscosity.

Chen and Pfender [12] pointed out the importance of non-continuum effects on the particle motion and proposed a correction term for drag coefficient \( C_D \) for \( 10^{-2} < Kn < 1 \).

\[
C_D = \frac{24}{Re} \left( \frac{\rho_{\text{Ar}} u_w}{\rho_{\text{Ar}} \mu_w} \right)^{-0.45} \times H^{-0.45}
\]

(7)

4.3. Particle trajectory and temperature history with free molecular model

At higher Knudsen numbers, the continuum concepts such as Fourier’s law, Eqs. [6,7], are no longer applicable. The flow situation in this case is almost free molecular flow region. The heat transfer rate from the plasma was evaluated using the model of a single particle in a rarefied gas. The heat transfer equation in a rarefied gas can be expressed as:

\[
q = q_{\text{neu}} + q_{\text{ion}} + q_{\text{elec}}
\]

(8)

where \( q \) is the total heat transfer rate from the plasma to a particle, \( q_{\text{neu}} \), \( q_{\text{ion}} \) and \( q_{\text{elec}} \) are the heat transfer rate owing to the neutral species, ions and electrons, respectively. The heat transfer rate owing to the neutral species can be expressed as:

\[
q_{\text{Ar}} = \frac{n_{\text{Ar}} v_{\text{Ar}}}{4} \alpha_{\text{Ar}} (2k_B T - k_B T_w)
\]

(9)

where \( k_B \) is the Boltzmann constant, \( T_w \) the particle temperature, \( n \) the number density, and \( v \) the first-order mean velocity. The accommodation coefficient \( \alpha_{\text{Ar}} \) was assumed to be 0.62 for the neutral species [13].

The heat transfer rate owing to the ions and electrons can be obtained from the following equation.

\[
q_{\text{ion}} + q_{\text{elec}} = \frac{n_{\text{ion}} v_{\text{ion}}}{4} \left( \alpha_{\text{ion}} (2k_B T - 2k_B T_w - e \phi_F) \right) + \alpha_{\text{elec}} (2k_B T - 2k_B T_w) + E_I
\]

(10)

where \( e \) is the unit charge, \( E_I \) the ionization energy, and \( \phi_F \) the float potential. The accommodation coefficients were assumed to be 0.48 for the ions and electrons [13].

The trajectory of the particle cannot be estimated from the continuum approach. Other approach based on free molecular flow has to be employed. The formula proposed by Chen and Pfender [12] is no longer applicable here because \( Kn \) is larger than 10 in this case, however no other useful formula has been found. Therefore, the particle velocity was assumed to be the same as the plasma velocity as the first approximation; this assumption was employed only for simplification, although the verification of the assumption is necessary. The particle trajectory was estimated using the model proposed by Chen and Pfender [12], even though this case is out of range of their model. The numerical simulations using their model showed that the velocity of a particle is the same as the plasma velocity after the injection.

4.4. Results of particle trajectory and temperature history

Trajectory and temperature history of single particle injected into thermal plasmas were calculated using the plasma temperature and velocity distributions. Particle temperature history for Si–Ti system was shown in Fig. 8. The feed powders of Ti and Si have similar temperature history, as well as the vaporization position. The vapor pressure distribution was estimated from the calculated temperature history of the injected particle. Simulation results of the vapor pressure and the saturated vapor pressure of Ti and Si are shown in Fig. 9. The similar temperature history of Ti and Si results in the coexistence of Ti and Si vapors in the plasma torch. Consequently the nucleation position of Ti is closed to that of Si, indicating that Ti and Si vapor nucleate in vapor phase simultaneously. Therefore, titanium silicide nanoparticles can be prepared successfully.

Simulation results for Mo–Si system are shown in Fig. 10. The calculated particle temperature history reveals that Mo and Si vapor coexist in the plasma torch. However, Mo vapor nucleates at relatively higher temperature than Si vapor. These results indicate that the control of condensation of Mo and Si vapor is important for the preparation of Mo silicide nanoparticles.

4.5. Homogeneous nucleation

The last task of the numerical simulation is the nucleation process of the evaporated species. Homogeneous
nucleation rate was proposed by Girshick et al. [14]. They derived the expression as an extension of kinetic nucleation theory. The proposed expression can be used over a wide range of physical conditions. Furthermore, the expression for homogenous nucleation rate was consistent with experimental data. Therefore Eq. (11) was used for the estimation of critical saturation ratio.

\[
J = \frac{\bar{b}_{ij} n_s^2 S}{12} \sqrt{\frac{\Theta}{2\pi}} \exp \left( \frac{-4\Theta^3}{27(ln S)^2} \right)
\]  

(11)

where \( n_s \) is the equilibrium saturation monomer concentration at temperature \( T \), \( S \) the saturation ratio, \( \bar{b}_{ij} \) the collision frequency function between \( i \)-mers and \( j \)-mers, and \( \Theta \) the dimensionless surface tension.

The dimensionless surface tension \( \Theta \) is given by:

\[
\Theta = \frac{\sigma s_1}{kT}
\]

(12)

where \( s_1 \) is the monomer surface area and \( \sigma \) the surface tension. The collision frequency function \( \bar{b}_{ij} \) can be estimated by Eq. (13) when the \( Kn \) is more than 10 [15].

\[
\bar{b}_{ij} = \left( \frac{3v_1}{4\pi} \right)^{1/6} \sqrt{\frac{6kT}{\rho_p} \left( \frac{1}{i} + \frac{1}{j} \right)} \times (i^{1/3} + j^{1/3})^2
\]

(13)

where \( v_1 \) is the monomer volume, and \( \rho_p \) particle mass density. In this model, the particle nucleation is due to the metal vapor collision, therefore \( i = j = 1 \).

Relationship between the nucleation rate and saturation ratio was shown in Fig. 11. The nucleation rate is strongly dependent on the surface tension and the saturation ratio. When the nucleation rate is over 1.0 cm\(^{-3}\) s\(^{-1}\), particle formation can be conveniently observed experimentally. Therefore, the corresponding value of saturation ratio is defined as the critical saturation ratio [15]. The critical saturation ratio of Si was estimated to be 4, while the other metals have the critical saturation ratio from 30 to 120.

The nucleation temperature at the critical saturation ratio was shown in Fig. 12 for constituent metals of silicide. The nucleation temperature of the metals except Si almost corresponds to the melting temperature, while Si has wide liquid range between the nucleation and melting temperature. Therefore, during the liquid stage of Si, other metal
vapor will be condensed on the liquid Si, resulting in better preparation of silicide.

For Mo–Si system, nucleation position of Mo is different from that of Si. In thermal plasmas, Mo nucleates faster than Si. After the nucleation and solidification of Mo, Si condensed around the solidified Mo particles. Therefore, quenching position has strong effect on the particle composition of molybdenum silicide nanoparticles.

5. Conclusions

Experiments and numerical simulations were performed to investigate the nanoparticle formation in thermal plasmas. The nucleation temperature of the metals is the key parameter in the nanoparticles formation. The nucleation temperature except Si almost corresponds to the melting temperature, while Si has wide liquid range between the nucleation and melting temperature, resulting in better preparation of silicide.

References

[1] M. Sakano, T. Watanabe, M. Tanaka, Numerical and experimental comparison of induction thermal plasma characteristics between 0.5 kHz and 4 MHz, J. Chem. Eng. Jpn 32 (1999) 619–625.
[2] M. Sakano, M. Tanaka, T. Watanabe, Application of radio-frequency thermal plasmas to recover materials from fly ash, Thin Solid Films 386 (2001) 189–194.
[3] T. Harada, T. Yoshida, T. Kozeki, K. Akashi, Co-condensation process of high temperature metallic vapors, J. Jpn Inst. Metals 45 (1981) 1138–1145.
[4] Y. Anekawa, T. Koseki, T. Yoshida, K. Akashi, The co-condensation process of high temperature metallic vapors, J. Jpn Inst. Metals 49 (1985) 451–456.
[5] T. Watanabe, H. Itoh, Y. Ishii, Preparation of ultrafine particles of Si base intermetallic compound by arc plasma method, Thin Solid Films 390 (2001) 44–50.
[6] T. Watanabe, A. Nezu, Y. Abe, Y. Ishii, Formation mechanism of electrically conductive nanoparticles by induction thermal plasmas, Thin Solid Films 435 (2003) 27–32.
[7] T. Watanabe, A. Kanzawa, T. Ishigaki, Y. Moriyoshi, Thermal plasma treatment of titanium carbide powders, J. Mater. Res. 11 (1996) 2598–2610.
[8] X. Chen, E. Pfender, Modeling of rf plasma torch with a metallic tube inseted for reactant injection, Plasma Chem. Plasma Process. 11 (1991) 103–128.
[9] J.P. Van Doormaal, G.D. Raithby, Enhancements of the SIMPLE method for predicting incompressible fluid flows, Num. Heat Transfer 7 (1984) 147–163.
[10] S.V. Patanker, Numerical Heat Transfer and Fluid Flow, McGraw-Hill, New York, 1980.
[11] X. Chen, E. Pfender, Effect of the Knudsen number on heat transfer to a particle immersed into a thermal plasma, Plasma Chem. Plasma Process. 3 (1983) 97–113.
[12] X. Chen, E. Pfender, Behavior of small particles in a thermal plasma flow, Plasma Chem. Plasma Process. 3 (1983) 351–366.
[13] T. Honda, T. Hayashi, A. Kanzawa, Heat transfer from rarefied ionized argon gas to a biased tungsten fine wire, Int. J. Heat Mass Transfer 24 (1981) 1247–1255.
[14] S.L. Girshick, C.P. Chiu, P.H. McMurry, Time-dependent aerosol models and homogeneous nucleation rates, Aerosol Sci. Technol. 13 (1990) 465–477.
[15] S.K. Friedlander, Smoke, Dust and Haze, Wiley, London, 1977.