Modeling of smoothening effect on morphologies of annealed submicron nickel particles used for electrically conductive adhesives

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Microelectronic packaging has been accelerating towards adoption of solutions that offer lower cost, higher electrical performance, and better reliability. Flip chip technology lends itself excellently to these goals. The development of anisotropic and isotropic conductive adhesives (ACA and ICA, respectively) as an alternative to solder bumps has received extensive attention in flip chip packaging as it offers an array of advantages such as finer pitch interconnects, green processes, low cost, and low temperature processing. Nickel, with its lower cost than that of silver and better thermal stability than that of copper, appears to be a viable candidate material for ICA and ACA applications. In the present study, a spiky surface morphology of nickel particles synthesized by means of a hydrothermal reduction method was clearly observed. The spiky morphology may have a detrimental effect on the conductivity of the ICA and ACA flip chip interconnect due to its smaller contact surface and propensity towards oxidation. The morphology of the nickel surface can be changed by annealing the particles between 270 and 360 °C for 4–12 h. A smoothening effect leading to more or less smooth spherical particles along with an increase in conductivity was observed after annealing at 360 °C for up to 12 h. An analytical model considering surface diffusion is established here to describe the temperature activated and energy minimization driven smoothening of the Ni particles. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356790]

I. INTRODUCTION

Electrically conductive adhesives (ECAs) play an increasingly important role in the design and production of electronic packages. Their advantages over the solder connection technology include fewer and cleaner processing steps and lower curing temperatures.[1–3] Isotropic and anisotropic conductive adhesives (ICA and ACA, respectively) constitute a group of ECAs which are gaining acceptance in the microelectronic industry. ICA relies solely upon the conductive fillers for electrical connectivity, whereas ACA consists of a polymeric matrix with conductive fillers that provide electrical connectivity only when the particles are crushed between the bumps of the flip chip. Details of ICA and ACA materials and applications are available in the literature.[4–6] Nickel is an excellent candidate material for ICA and ACA applications because of the numerous advantages it possesses, such as good chemical stability and slower oxidation compared to copper. Although it has a higher electrical resistivity compared to silver (about four times that of silver), its cost is 12 times lower than that of silver.[2]

A number of physical and chemical techniques can be used to produce metal particles in the nanosized regime. Some examples include photolytic reduction, radiolytic reduction, solvent extraction reduction, hydrothermal reduction, and microemulsion technique.[7–9] Among the chemical methods, the reduction of a metal salt or oxide by an appropriate reducing agent is frequently employed. Properties of the product are strongly influenced by the reactants which include the metallic precursor, the reducing agent, and the solvent medium. Properties of the reaction medium such as basicity, polarity, viscosity, and boiling point will also affect the reaction to a great extent.[10]

Temperature has the most profound influence on the coefficients and diffusion rates. Annealing provides an effective approach to modify the morphology and/or phase of the microstructures, thus tuning the materials' properties. One of the key factors leading to the morphology change of a particle is surface diffusion. Surface diffusion, or atom and molecular dynamics at surfaces, is a subject of considerable importance in surface and nanosciences since many surface phenomena involve mass transport and dynamic fluctuations of atoms, cluster, and molecules.[11] These phenomena include surface reconstruction, crystal growth and thin film epitaxy, shape change and sintering, adsorption and desorption, and surface promoted chemical reactions.

This paper reports on simulating the effect of the change

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of morphology of the synthesized nickel particles. The methodology presented here may also be applied to other materials.

II. EXPERIMENTAL PROCEDURES

Nickel particles were synthesized by means of a hydrothermal reduction method. To obtain pure nickel particles, aqueous nickel sulphate had to be reduced using aqueous hydrazine solution. The concentration of nickel sulphate will determine the size of nickel particles. By varying the Ni salt concentrations, Ni particle sizes ranging from about 400 nm to 1 μm could be obtained. Observed under scanning electron microscope (SEM), Ni particles obtained from different precursor concentrations had spiky surfaces on generally spherical shaped particles. This surface phenomenon could be due to the preferential growth of Ni in a particular direction during synthesis.

Nickel particles were heat treated at 270, 310 and 360 °C for durations of 4, 8, and 12 h. The nickel particles were then incorporated into a thermoset system for thermal conductivity measurement. The details for the nickel synthesis and the following annealing process have been given elsewhere.[12,13] The surface area of the Ni particles was also measured by the Brunauer-Emmett-Teller (B.E.T.) technique using a Micromeritics ASAP 2000 analyzer, and the particle size was measured using Fritsch particle sizer analysette 22 compact.

III. ANALYTICAL MODELING

In order to understand the underlying mechanism for the smoothening effect of nickel particles during annealing, an analytical model considering surface diffusion is established. From the thermodynamics point of view, smoothening is favorable due to the decrease of surface energy through surface diffusion.[14,15] This surface diffusion is locally generated by the gradient of curvature. Namely, local input of Laplace tension in the Gibbs energy per atom (i.e., chemical potential) is expressed as

$$\Delta\mu = \Omega\frac{\gamma}{R}, \tag{1}$$

where $\Delta\mu$ is the potential energy (J), Ω is the atomic volume (1.09×10^{-29} m^3), γ is the surface energy ($1.7\ J/\text{m}^2$), and R is the curvature ($0.6\ \mu\mathbf{m}$).Thus, force per atom (N), arising from the change of curvature $1/R$, is equal to

$$F_s = -\frac{\partial}{\partial s}\left(\Omega\frac{\gamma}{R}\right), \tag{2}$$

where ∂s is the change of curvature.

So, the surface diffusion flux density (J_s) is

$$J_s = \frac{C_S D_S}{k_B T}F_s = -\frac{C_S D_S}{k_B T}\frac{\partial}{\partial s}\left(\Omega\frac{\gamma}{R}\right), \tag{3}$$

where C_S is the concentration (8.908 kg/m^3), D_S is the diffusion coefficient (3.5×10^{-24} m^2/s), k_B is the Boltzmann constant (1.38×10^{-23} J/K), and T is the temperature (633 K).

Shape evolution of the surface is determined by the local divergence of surface fluxes. Namely, the divergence of surface flux density is proportional to velocity, which is normal to the profile,

$$V_n = -\Omega\frac{\partial J_s}{\partial s}. \tag{4}$$

Combining Eqs. (4) and (3), we obtain

$$V_n = -\Omega\frac{\partial J_s}{\partial s} = \frac{\Omega C_S D_S}{k_B T}\frac{\partial^2}{\partial s^2}\left(\Omega\frac{\gamma}{R}\right). \tag{5}$$

If we use Cartesian coordinates, the curvature (k, i.e., the inverse of the radius) is

$$\frac{1}{R} = \frac{d^2y/dx^2}{[1+(dy/dx)^2]^{3/2}}. \tag{6}$$

Cartesian components of the local velocity are

$$V_{nx} = -V_n\sin\theta = -V_n\frac{dy/dx}{[1+(dy/dx)^2]^{1/2}}, \tag{7}$$

$$V_{ny} = V_n\cos\theta = V_n\frac{1}{[1+(dy/dx)^2]^{1/2}}. \tag{8}$$

The commercial software MATLAB combined with finite difference method is used to model the change of morphology of the nickel particle. The expression in finite differences for Eq. (6) is

$$\begin{aligned} k_i = \frac{1}{R_i} &= \frac{\{[(y_{i+1}-y_i)/(x_{i+1}-x_i)-(y_i-y_{i-1})/(x_i-x_{i-1})]/[(x_{i+1}+x_i)/2-(x_i+x_{i-1})/2]\}}{\{1+[(y_{i+1}-y_{i-1})/(x_{i+1}-x_{i-1})]^2\}^{3/2}} \\ &= \frac{2(x_{i+1}-x_{i-1})^2[(y_{i+1}-y_i)(x_i-x_{i-1})-(y_i-y_{i-1})(x_{i+1}-x_i)]}{(x_{i+1}-x_i)(x_i-x_{i-1})[(x_{i+1}-x_{i-1})^2+(y_{i+1}-y_{i-1})^2]^{3/2}}. \end{aligned} \tag{9}$$

The derivative of the function k along the profile is

$$\left.\frac{\partial k}{\partial s}\right|_{i+1/2} \cong \frac{k_{i+1}-k_i}{[(y_{i+1}-y_i)^2+(x_{i+1}-x_i)^2]^{1/2}}, \tag{10}$$

and the second derivative may be written as

$$\left.\frac{\partial^2 k}{\partial s^2}\right|_i \cong \frac{(\partial k/\partial s)|_{i+1/2} - (\partial k/\partial s)|_{i-1/2}}{(1/2)[(y_{i+1}-y_{i-1})^2+(x_{i+1}-x_{i-1})^2]^{1/2}}$$
$$= 2\frac{\{(k_{i+1}-k_i)/[(y_{i+1}-y_i)^2+(x_{i+1}-x_i)^2]^{1/2}\} - \{(k_i-k_{i-1})/[(y_i-y_{i-1})^2+(x_i-x_{i-1})^2]^{1/2}\}}{[(y_{i+1}-y_{i-1})^2+(x_{i+1}-x_{i-1})^2]^{1/2}}. \tag{11}$$

Numerically, the set of differential equations for arrays x[i] and y[i] is

$$\frac{dx[i]}{dt} = -V_n[i]\frac{(y[i+1]-y[i-1])}{[(x[i+1]-x[i-1])^2+(y[i+1]-y[i-1])^2]^{1/2}}, \tag{12}$$

$$\frac{dy[i]}{dt} = V_n[i]\frac{(x[i+1]-x[i-1])}{[(x[i+1]-x[i-1])^2+(y[i+1]-y[i-1])^2]^{1/2}}, \tag{13}$$

with

$$V_n[i] = \left.\frac{\partial^2 k}{\partial s^2}\right|_i$$
$$=2\frac{\{(k[i+1]-k[i])/[(y[i+1]-y[i])^2+(x[i+1]-x[i])^2]^{1/2}\} - \{(k[i]-k[i-1])/[(y[i]-y[i-1])^2+(x[i]-x[i-1])^2]^{1/2}\}}{[(y[1]-y[i-1])^2+(x[i+1]-x[i-1])^2]^{1/2}}.$$

The above equation is solved by commercial MATLAB using nondimensional time of 1×10^6 iterations.

IV. RESULTS AND DISCUSSION

A. Experimental results

Nickel particles with a spiky surface were observed after synthesis. The nickel particles are more or less spherical in shape with a spiky morphology. Upon exposure to annealing, a change in this spiky morphology was observed. The effects of the diminishing spikes were clearly seen in the nickel powders annealed at 360 °C for 4, 8, and 12 h. Figures 1–4 show that the spikes that were present before heat treatment were almost all gone after annealing for 12 h at 360 °C. The resistance of samples made from unannealed Ni particles was of the order of $5\times10^3\,\Omega$. The resistance was found to decrease to about 90 Ω upon a 4 h anneal at 270 °C and it further reduced to under 2 Ω upon a 12 h anneal at 360 °C (Fig. 5). Annealing is thought to minimize crystalline defects that serve as scattering centers for conduction electrons in metals, which in turn is expected to increase conductivity. The surface areas of the Ni particles before and after study as measured by the B.E.T technique are presented in Fig. 6. The smoothening of the spiky surfaces with annealing leads to an overall reduction in surface area, thus increasing the contact area between adjacent particles, which in turn improves electrical conductivity of the samples. Particle size is not affected by the annealing process (Fig. 7) as the temperature used was not high enough to cause any agglomeration, grain growth, or sintering of the particles.

B. Modeling results

The modeled particle with spiky surfaces showed toning down of the spikes with progressive annealing time (Fig. 8). The modeling results compare favorably with the SEM images presented in Fig. 1. It is observed that the spikes go

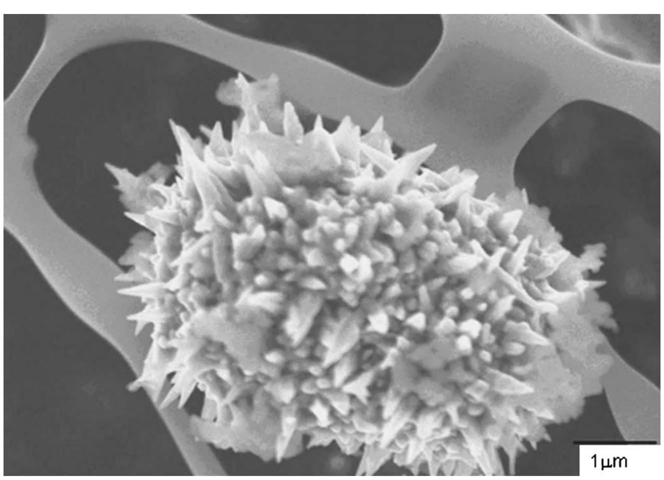

FIG. 1. Synthesis of nickel particle (35 000×).

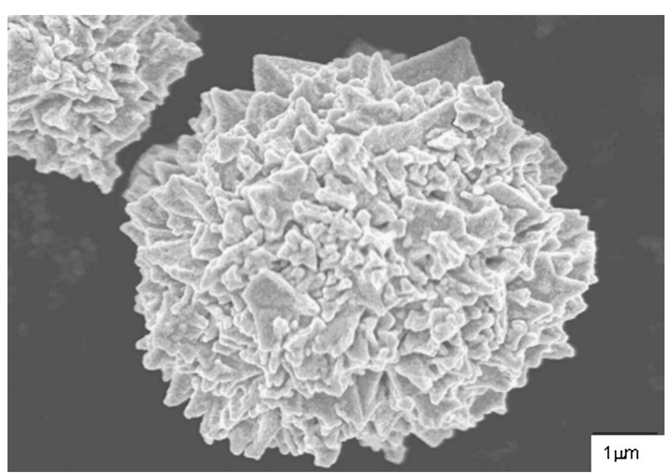

FIG. 2. Annealed at 360 °C for 4 h (35 000×).

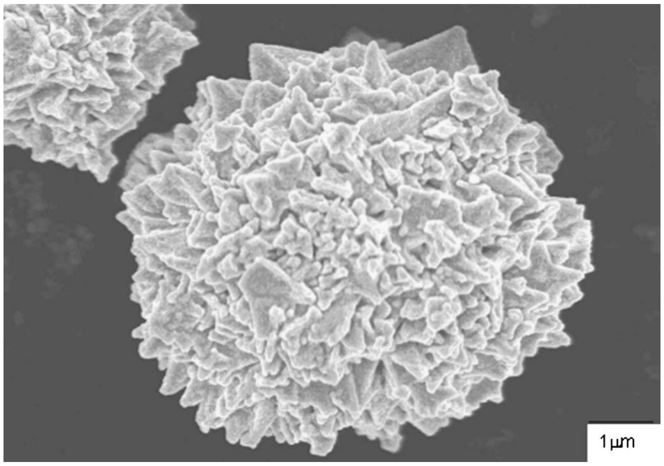

FIG. 3. Annealed at 360 °C for 8 h (35 000×).

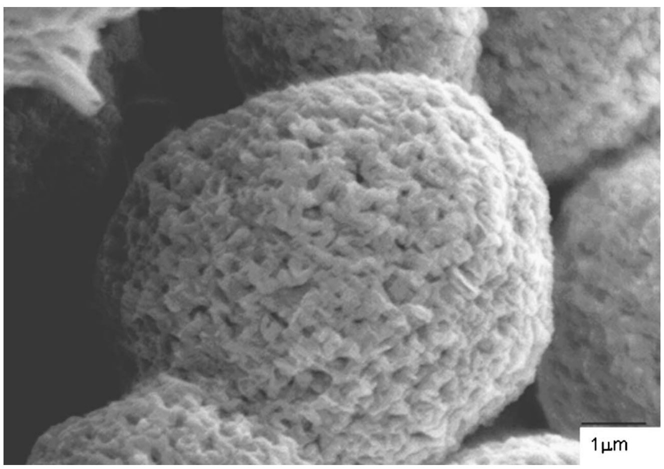

FIG. 4. Annealed at 360 °C for 12 h (35 000×).

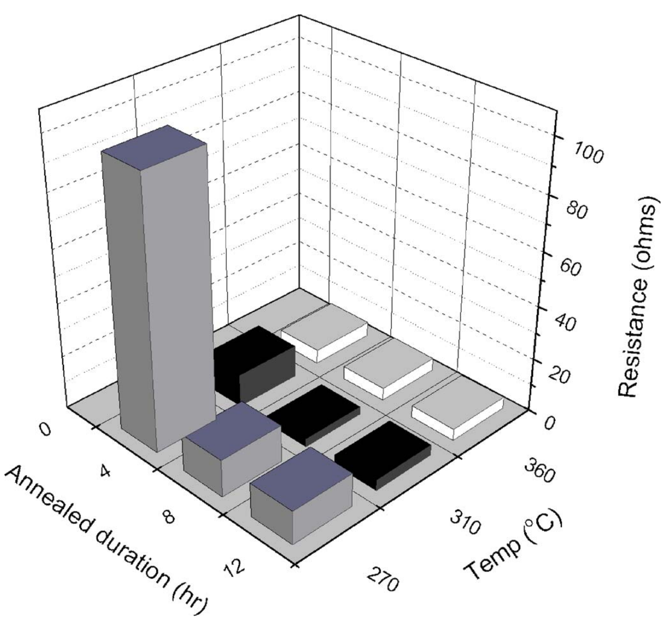

FIG. 5. The electrical resistance of ECAs with 75 wt % of Ni particles annealed at different temperatures and times.

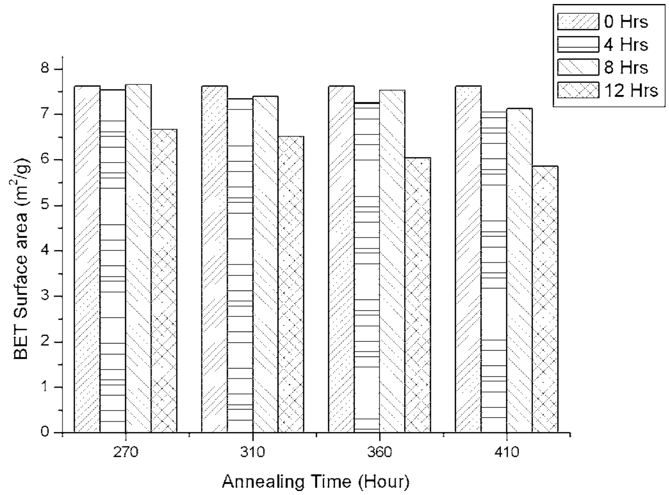

FIG. 6. Surface area of Ni particles before and after annealing.

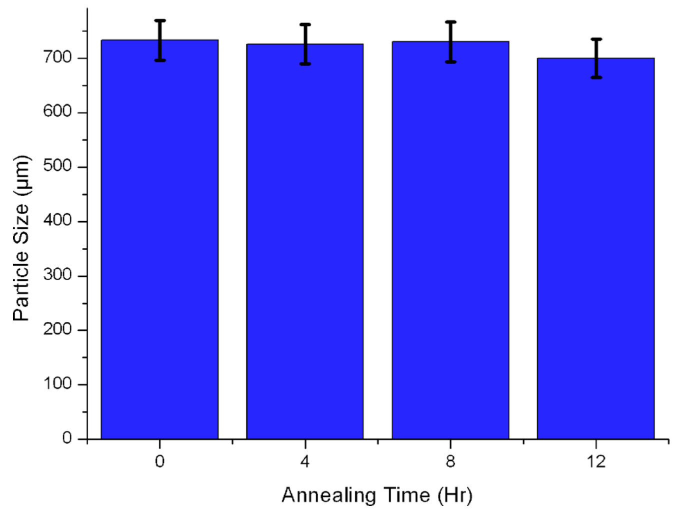

FIG. 7. Particle sizes of the annealed Ni particles.

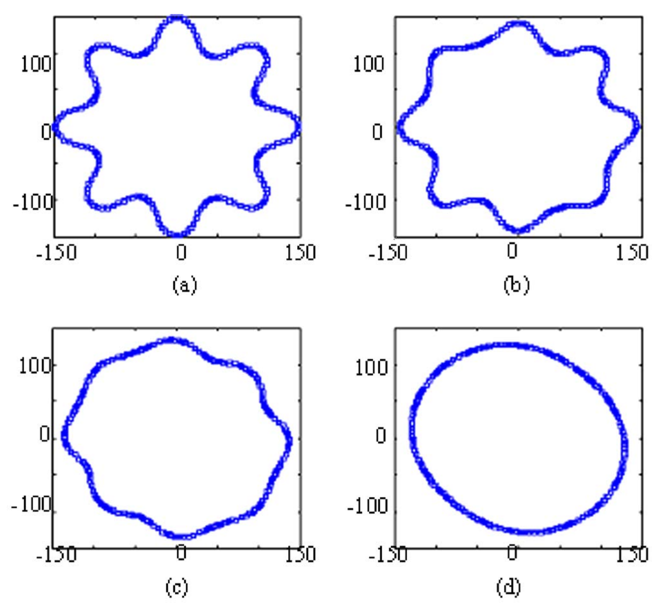

FIG. 8. Modeling of particles at 360 °C, at different annealing times of (a) 0 h, (b) 4 h, (c) 8 h, and (d) 12 h

through a smoothening process until they more or less disappear after a 12 h anneal at 360 °C. It is also observed that, in agreement with the experimental data, the overall size of the Ni particles does not change. Similar methodologies may be applied to other material systems and also to planar surfaces to simulate the morphological changes that may occur driven by diffusion and minimization of energy considerations.

V. CONCLUSIONS

Submicometer sized Ni particles synthesized for ACA and ICA applications in this study were found to have a spiky surface morphology. This morphology has a very detrimental effect on conductivity and a surface modification was therefore pursued by an annealing treatment at 270–360 °C for 4–12 h. Exposure to a 12 h anneal at 360 °C led to a smoothening of the Ni particles and also reduced its resistance from $5\times10^3\ \Omega$ to under 2 Ω. The change in morphology did not lead to agglomeration or increase in particle sizes as confirmed by B.E.T and particle size measurements. An analytical model considering surface diffusion was established to account for the temperature activated and energy minimization driven smoothening of the Ni particles.

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