Application of the Taguchi Method to Optimize Graphene Coatings on Copper Nanoparticles Formed Using a Solid Carbon Source

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Graphene has attracted much recent interest as an electronic material due to its large electron mobility. Large-area graphene has been synthesized using chemical vapor deposition (CVD). However, it is difficult to apply this process to grow graphene on nanoparticles (NPs) because of their small radius of curvature, which results in a large defect density. In this work, we used the Taguchi method to optimize the deposition of graphene on nanoparticles. We used polyvinylpyrrolidone (PVP) to coat copper NPs via CVD and optimized the process conditions using a minimal number of experiments. The PVP served as the solid carbon source, forming graphene when heated to 875°C. To improve the quality of the graphene coatings on the Cu NPs, the following process parameters were varied: gas conditions (ratio of Ar to H₂), process time and temperature, the amount of PVP solution, and the molecular weight of PVP. We identified optimal process conditions using only eight experiments. Raman spectroscopy was used to analyze the quality of the graphene coatings by comparing two-dimensional (2D) spectra and I_D/I_G ratios of the different coatings. A decrease in I_D/I_G , in combination with sharper Raman bands, is indicative of the thickness and crystal quality of the graphene layer. The quality of the graphene layer was also evaluated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

The optimal conditions for the formation of graphene-coated Cu NPs were: a temperature of 875°C, a deposition time of 2 minutes, an Ar-to-H₂ ratio of 1:1, PVP with a molecular weight of $M_w = 3,500$ (K-12) during the polyol process, and a 50-wt.% PVP solution with $M_w = 45,000$ (K-30). Using the Taguchi method, we identified trends relating defect density versus process conditions and successfully obtained a graphene coating with a minimal defect density. [doi:10.2320/matertrans.M2016011]

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1. Introduction

Conductive nanoinks are suitable for the formation of fine patterns, exhibit good dispersibility in solvents, and have been applied in various fields of electronics. However, the materials used in conductive nanoinks are limited mainly to expensive metals such as Ag, Au, Pt and Pd^{1–3}. Copper has a large electrical conductivity, and is relatively inexpensive^{4,5}. Hence, there is significant interest in replacing these noble metals with Cu.

With Cu-based nanoinks, preventing aggregation and oxidation of the nanoparticles (NPs) is important⁶. There exist various techniques to inhibit the oxidation of copper NPs, including coating them with noble metals^{7,8}, self-assembled monolayers^{9,10}, polymers¹¹, or carbon-based materials^{12,13}. Polyvinylpyrrolidone (PVP) makes a particularly interesting coating for the prevention of copper NP oxidation. However, PVP-coated copper NPs are not readily dispersed in solvents and a dispersant must be added to the nanoink. This makes low-temperature sintering difficult because the presence of the dispersant can result in necking among the copper NPs. The use of carbon-based coating materials can also prevent the oxidation of the Cu NPs¹⁴. However, amorphous carbon is electrically insulating, which is problematic for conductive nanoinks.

For these reasons, graphene is particularly interesting as a coating material for the prevention of Cu NP oxidation in conductive nanoinks. Graphene can prevent not only oxida-

tion from air^{14,15}, but also its large electrical and thermal conductivities make it suitable for applications in electronic devices^{16,17}. However, graphene is prone to structural defects due to the adsorption of contaminants onto its surface and breaking of the hexagonal bonding structure, which reduces the electrical conductivity, especially with very thin layers of graphene^{17–20}.

A source of carbon is required to form graphene. Commonly used sources include CH₄ gas, which forms graphene via chemical vapor deposition (CVD), and enables large-area depositions with high quality^{21–24}. However, with a gaseous carbon source, the efficiency of the reaction is low and there is a risk of explosion. A gas source can also be used to form graphene on Cu NPs, but tends to accelerate necking among the NPs²⁵. The purpose of this study was to demonstrate a PVP coating layer as a solid carbon source. It has been shown that it is possible to convert some of the polymer into graphene at 900°C^{25–27}, which is suitable for the CVD deposition of graphene²⁵.

Raman spectroscopy can be used to confirm the presence of graphene. The Raman spectra of graphene exhibit specific peaks corresponding to the D, G and 2D bands. These are related to the A1' vibrational mode, which is indicative of the symmetry of the hexagonal lattice. A peak for the D band appears when the symmetry of this mode is broken by structural defects. In other words, the presence of a D peak indicates that the graphene is defect rich or that there is structural disorder²⁸. The G peak corresponds to an optical phonon mode, whereby adjacent carbon atoms vibrate in opposite directions. The E_{2g} vibrational mode is also related to symme-

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try and this peak is associated with vibrations of sp^2 -hybridized bonds, commonly found in carbon-based materials²⁹. The 2D band is related to secondary Raman scattering. With single- or double-layer graphene, the 2D band peak is both intense and sharp. If the graphene has three or more layers, this peak broadens because of overlap between the layers^{28,30,31}. For these reasons, the intensity ratio I_D/I_G corresponds to the defect density, and the ratio I_{2D}/I_G is indicative of the number of layers.

Taguchi methods are used to identify trends using a minimum number of experiments where there are many variables in a given experiment. Taguchi methods have been applied in several research areas as a means of optimizing conditions. A Taguchi method is characterized by five stages: 1) problem identification, 2) decisions about the control and signal factors, levels and objectives, 3) design of experiment, 4) experimental implementation, and 5) analysis of the results³². First, an understanding of the variables is required to identify an appropriate control factor. In general, the variables should be adjusted as factors that are controlled during the experiments. A signal factor was not considered here as this is a non-adjustable variable. After a variable had been selected in step 2, we established the number of levels as 2–4 per variable. It is also important to select appropriate experimental objectives, and three is common. For a given parameter, the optimum result can be characterized in three ways: either smaller is better, on-target is better, or larger is better. For the first case, where smaller is better, a smaller experimental result represents higher quality³³. For the second case, where nominal is better, good results are generally obtained when the result is closer to the target, with minimal variance. For the third case, where the optimal value is larger³⁴, the value improves as it increases. In this manner, the trends used to identify the optimal conditions can be found by sorting the values of the variables and by running additional experiments to confirm predictions.

Here, a PVP coating was layered onto Cu NPs using a polyol method. The PVP was then used as a solid carbon source and converted to graphene via CVD. We investigated the influence of the quantity and molecular weight of the PVP solution, the atmospheric conditions, the process time, and the process temperature on the quality of the graphene coatings formed on Cu NPs, while preventing necking of the NPs. The quality of the graphene layers was characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman spectroscopy.

2. Experimental

2.1 CVD coating process

Copper NPs were synthesized with a diameter of ~100 nm using a polyol method to form PVP-coated NPs^{35,36}. A diethylene glycol (DEG, Extra pure, 1 L, JUNSEI, Japan) solution was used during the polyol process and was subsequently removed using methanol and centrifugation. The PVP solution was formed using a solution of PVP powder (SHOWA, K-30, Japan) in chloroform (JUNSEI, Japan) and dimethylformamide (DMF) (DAEJUNG, Korea) at a mass ratio of 5:5:1. Finally, PVP solutions, from 30 wt.% to 50 wt.%, were added into the solution to minimize amount of necking among par-

Fig. 1 Schematic diagram of the process used to form graphene coatings on copper nanoparticles.

Fig. 2 (a) Schematic diagram of the graphene coating before heating. (b) Formation of an amorphous carbon layer via thermal decomposition of C-N bonds. (c) Alignment of carbon chains on the surface of the nanoparticles. (d) The resulting graphene-coated copper nanoparticles.

ticles during the CVD process. The resulting mixture was deposited on SiO_2 substrates with planar dimensions of $1.5 \times 1.5 \text{ cm}^2$, as shown in Fig. 1, and dried in a glove box for 2 hours in an Ar atmosphere. The PVP layer was then converted to graphene via CVD in a quartz chamber. The PVP solution inhibited necking of adjacent copper NPs. The heating rate of the CVD system was $60^\circ\text{C}/\text{min}$. The NPs were allowed to cool to room temperature following this heating process. The process temperature, process time, and ratio of Ar and H_2 gases were varied during the CVD process. The concentration and molecular weight of the PVP solution that was coated onto the Cu NPs, were controlled.

Figure 2 shows the mechanism of graphene formation on Cu NPs via CVD. When the PVP layer was heated above 850°C in Ar and H_2 , bonds between nitrogen and the carbon chain of PVP thermally decomposed and the coating layer was transformed into amorphous carbon. The sample was then allowed to cool to room temperature. The amorphous carbon layer aligned and was thereby converted to graphene, as shown in Fig. 2(c).

The resulting coating layers were characterized using TEM (JEM-2100F HR, JEOL) to measure layer thickness. The degree of necking between Cu NPs was investigated using SEM (S4800, Hitachi). The conversion of the polymer layer to graphene was investigated using Raman spectroscopy (RM 1000, RENISHAW).

2.2 Design of experiments

Table 1 lists the variables used in the conversion of the PVP coating to graphene. The ranges of experimental conditions indicated in the table were determined in a preliminary study by Cho. *et al.*³⁷. Three different gas compositions were used at two different temperatures, times, concentrations of PVP, and molecular weights of PVP. As the number of param-

eters increased, the number of experiments required to consider each factor increased exponentially. Thus 8 parameters, each of which is evaluated at two levels, would require a time-consuming $2^8 = 256$ experiments. However, the Taguchi method allows for a fractional design that reduces the number of experiments by disregarding interactions among the various factors³². This makes the Taguchi method suitable for investigating trends with many variables.

Argon and hydrogen atmospheres are typically employed in the CVD growth of graphene. The densities of defects, edge dislocations, and wrinkles on the graphene surface increase as the hydrogen fraction decreases³⁸. In our experiments, we varied the process temperature, the quantity of PVP in the solution, and the process time to minimize necking. We also used low-molecular-weight PVP in order to minimize the thickness of the graphene layer.

The gas ratio was varied to minimize the density of structural defects that result from hydrogen gas adsorption onto the surface of graphene. We varied the Ar:H₂ ratio through 1:1, 1:0.75, and 1:0.5. The total quantity of gas was fixed at 140 sccm. PVP can be converted to graphene at temperatures >850°C²⁵ and we evaluated process temperatures of 875°C and 900°C. The CVD process times were 2 and 3 min, and the concentration of the PVP solution was either 30 or 50 wt.%. The molecular weights of PVP were K-12 (3,500) or K-30 (45,000). Normally, this parameter space would require a total of ($2^5 \cdot 3^1$) = 96 experiments for a full evaluation. However, the Taguchi method enabled us to investigate these parameters using only eight experiments (Table 2).

Table 1 Variables in the Taguchi method.

Variable	Levels		
	1	2	3
Gas Ratio of Ar:H ₂	1:1	1:0.75	1:0.5
Temperature (°C)	875	900	
Time (min)	2	3	
PVP solution (wt.%)	30	50	
PVP molecular weight	3,500 (K-12)	45,000 (K-30)	

Table 2 Design of experiments.

Experiment	Variables				
	Gas Ratio of Ar:H ₂	Temperature (°C)	Time (min)	PVP solution (wt.%)	PVP Molecular weight
D1	1:1	875	2	30	45,000 (K-30)
D2	1:1	875	2	50	45,000 (K-30)
D3	1:1	900	3	30	45,000 (K-30)
D4	1:0.75	900	3	30	45,000 (K-30)
D5	1:0.5	900	3	30	45,000 (K-30)
D6	1:0.5	900	2	30	45,000 (K-30)
D7	1:0.5	875	2	30	45,000 (K-30)
D8	1:1	875	2	50	3,500 (K-12)

3. Results and Discussion

3.1 CVD process conditions

To apply the Taguchi method to our experimental results, we must convert the measured ratios I_D/I_G to signal-to-noise (S/N) ratios. Quantification of the S/N ratio facilitates the simple identification of potential improvements.

Figure 3 shows Raman spectra for the 8 samples listed in Table 2. The D, G, and 2D peaks were observed for all samples. The peak corresponding to the D band appears due to the curvature of the graphene and structural defects caused by absorption of atoms on the graphene surface. The Cu NPs used here were spherical, resulting in a high degree of surface curvature and a correspondingly strong D band peak²⁵. The presence of a G band peak indicates that all of the samples were carbon-based materials. The ratio I_D/I_G was used as an indirect measure of the defect density in the graphene coating. Table 3 lists the S/N ratios obtained from all 8 samples.

The ratio I_D/I_G can be converted to an S/N ratio as follows³³:

$$(S/N)_{\text{smaller-is-better}} = -10 \log_{10} \left[1/n \sum_{i=1}^n (Y_i^2) \right] \quad (1)$$

3.2 Optimization

Figure 4 shows the average S/N ratio corresponding to the level of each of the variables, as calculated using I_D/I_G . Figure 4 shows I_D/I_G for temperatures of 875°C and 900°C. The DOE samples D1, D2, D7, and D8 were processed at 875°C

Fig. 3 Raman spectra of samples formed with the process conditions listed in Table 2.

Table 3 Signal-to-noise (S/N ratios) calculated from I_D/I_G .

Experiments	I_D/I_G ratio	
	Result	S/N (dB)
D1	0.70	3.10
D2	0.70	3.10
D3	0.71	3.01
D4	0.70	3.07
D5	0.72	2.88
D6	0.74	2.63
D7	0.71	3.00
D8	0.68	3.35

Fig. 4 Signal-to-noise (S/N) ratios calculated using I_D/I_G for the samples listed in Table 3.

and the corresponding S/N ratios were 3.10, 3.10, 3.00, and 3.35, respectively. The mean of these data is 3.14, as shown in Fig. 4.

The condition resulting in the largest S/N ratio for each variable was considered optimal, corresponding to a lower defect density or thinner graphene coating. The minimal defect density was observed under the following process conditions: a gas mixture of Ar:H₂ = 1:1 (S/N ratio of I_D/I_G = 3.14), a process temperature of 875°C (S/N ratio of I_D/I_G = 3.14), a processing time of 2 min (S/N ratio of I_D/I_G = 3.03), a 30 wt.% PVP solution (S/N ratio of I_D/I_G = 3.22) and a molecular weight of PVP of 3,500 (i.e., K-12) (S/N ratio of I_D/I_G = 3.35), as shown in Fig. 4.

Figure 5 shows the different influences between the maximum and minimum values of each parameter for both I_D/I_G . These data determine the degree of influence of each parameter. The variable with the greatest impact on I_D/I_G was the molecular weight of the PVP. Based on these data, condition A1 exhibited the lowest defect density in graphene coating layers. Therefore, the optimal conditions were as follows: a molecular weight of PVP during the polyol process of M_w = 3,500 (K-12) and 30 wt.% PVP solution with M_w = 45,000 (K-30), a 1:1 Ar:H₂ ratio during CVD, and a process time of 2 min at 875°C.

3.3 Additional experiments in accordance with the amount of PVP solution

Section 3.2 summarized the optimum conditions for a minimum number of defects in the graphene coating layer (Table 4). To confirm this optimum condition experimentally, additional experiments, such as increasing the wt.% of PVP solution to minimize the necking in the Cu NPs, were performed to determine whether it could be applied to conductive copper nanoink with a graphene coating on Cu NPs (Table 5).

Figure 6 shows copper nanoparticles that were coated with a graphene coating layer via a CVD process, based on A1

The degree of influence of the control factors based on I_D/I_G ratio. Fig. 5 Degree of influence of the variables, based on I_D/I_G ratio.Table 4 Optimized conditions based on S/N ratios calculated from I_D/I_G .

Optimized condition	Variables				
	Gas Ratio of Ar:H ₂	Temperature (°C)	Time (min)	PVP solution (wt. %)	PVP Molecular weight
(A1) Smaller Defect	1:1	875	2	30	3,500 (K-12)

Table 5 Conditions for additional experiments based on S/N ratios calculated from I_D/I_G .

Experiment	Variables				
	Gas Ratio of Ar:H ₂	Temperature (°C)	Time (min)	PVP solution (wt. %)	PVP Molecular weight
A1	1:1	875	2	30	3,500 (K-12)
A1-2	1:1	875	2	40	3,500 (K-12)
A1-3, D8	1:1	875	2	50	3,500 (K-12)

Fig. 6 Raman results and scanning electron microscopy (SEM) micrographs of graphene-coated copper nanoparticle form, based on (A1), (A1-2), and (A1-3, D8) conditions.

condition. Moreover, Raman analysis showed that the copper particles coated with the optimum A1 coating condition (based on the Taguchi method) showed the lowest I_D/I_G ratio, consistent with the Taguchi analysis, minimizing defect conditions. However, the size of the particles grew from 100 nm to 1 μm-scale after the CVD process. The coarsening of parti-

Fig. 7 Transmission electron microscopy TEM micrographs of (a) graphene-coated copper nanoparticle and (b) graphene layers based on (A1-3, D8) condition (the inset is a magnified TEM image of graphene coating layers).

cles may be due to there not being enough PVP solution to coat the surface of Cu NPs to prevent necking among particles during the CVD process. To overcome this, the amount of PVP solution was increased to 40 and 50 wt.%, to ensure sufficient PVP solution to prevent necking among particles during the CVD process. The microstructures of Cu NPs in Fig. 6 showed that the shape of copper nanoparticles was maintained with extra PVP solution of 40 (A1-2) and 50 wt.% (A1-3, D8) after processing at 875°C. When the polymer was converted to a graphene coating layer, copper nanoparticles maintained their shapes due to this coating layer. These can be expected to prevent oxidation of copper nanoparticles because the coating layer is entirely wrapped around the surface of particles. Moreover, the I_D/I_G ratios for both A1-2 and A1-3 samples with a graphene coating on the copper particles were measured to be 0.68.

In particular, Cu NPs with 50 wt.% PVP solution (A1-3) (D8) showed a more uniform size distribution of Cu NPs than that of A1-2. Thus, adding extra PVP solution increased the I_D/I_G ratio slightly, while minimizing necking and preventing coarsening. This slight increase in I_D/I_G ratio agrees with the Taguchi analysis results in Fig. 4. However, Taguchi analysis results focus only on the quality of the graphene and not on necking conditions. Because minimizing necking among Cu NPs is important for applications, such as of conductive nanoink as much as I_D/I_G ratio for the quality of graphene coating, Cu NPs with extra 50 wt.% of PVP solution (A1-3) were found to be the optimum coating condition with a low I_D/I_G ratio.

Additionally, TEM analysis was performed to confirm graphene coating layers onto Cu NPs to be synthesized based on the optimal conditions as shown in Fig. 7. It has observed that the graphene-coated Cu NPs had a size of 80 nm in diameter and the graphene coating surrounded the entire surface of the particles. The thickness of graphene coating onto copper nano-particle was measured to be less than 2.8 nm and it was confirmed that the graphene coating layer was composed of the five layers (see the inset of TEM image in Fig. 7(b)). This result is consistent with the total thickness of the graphene coating measured in Fig. 7(b), being 1.73 nm, given that a single layer of graphene is known to be 0.37 nm³⁹.

4. Conclusions

The Taguchi method was used to identify optimized process conditions for the fabrication of graphene coatings on Cu

NPs using a minimal number of experiments. Graphene coatings were formed on Cu NPs using a solid carbon source via CVD. The Taguchi method was used to derive S/N ratios from the I_D/I_G ratios of Raman results. The ratio I_D/I_G is related to the defect density.

Based on the Taguchi method, the final optimum coating conditions for graphene coating on Cu NPs were as follows: a process temperature of 875°C, a process time of 2 min, a Ar:H₂ ratio of 1:1, a PVP molecular weight of $M_w = 3,500$ (K-12) during the polyol method, and a 30-wt.% PVP solution with $M_w = 45,000$ (K-30). However, a significant degree of necking was observed when the optimum conditions were used to coat Cu NPs with graphene. Next, further experiments were performed to add 40 and 50 wt.% PVP solutions into Cu NPs. As a result, necking among Cu NPs was reduced significantly using 50 wt.% PVP solution while keeping a low I_D/I_G ratio for Raman analysis. Finally, graphene coating on Cu NPs using 50 wt.% PVP solution showed a uniform distribution of Cu NPs, successfully preventing coarsening among NPs, with an I_D/I_G ratio of 0.68. Thus, the Taguchi method was used successfully to identify optimized process conditions for the formation of graphene-coated Cu NPs.

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