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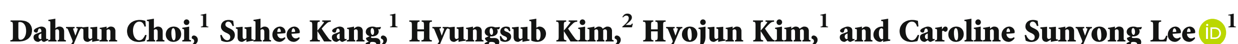
Research Article

Rapid Formation of Kinetically Sprayed Cu-Sn Intermetallic Film



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The kinetically spraying method was used to fabricate an in situ copper- (Cu-) tin (Sn) intermetallic compound (IMC) film with its thickness of approximately 1 μm using a Cu-Sn mixed powder. Microsized Cu (~5 μm) and Sn (~10 μm) powders were mixed at its ratio of 45 : 55 wt.%, respectively, and then deposited onto a silicon substrate, forming an IMC layer. The actual composition of the deposited film was measured to be at a Cu : Sn ratio of 36 : 64 wt.% (in situ kinetically sprayed at 200°C). This kinetically sprayed process uses the energy source of collision and heat energy simultaneously, leading to the formation of an IMC phase. The IMC phase of Cu_6Sn_5 was formed successfully within 3 minutes of in situ deposition. Moreover, we obtained a Cu_6Sn_5 phase when the thin film was annealed in a furnace for 1 hour immediately after kinetically spraying at room temperature. However, an IMC phase was not formed in the thin film when kinetically sprayed at room temperature followed by heating on a hot plate for 3 minutes. It seems that the simultaneous supply of collision and heat energy is crucial to result in phase formation. Therefore, we have proven that the kinetically spraying process is capable of fabricating a super-thin layer of IMC film within a short time.

1. Introduction

Copper- (Cu-) tin (Sn) intermetallic compounds have numerous advantages that have led to their being widely used in various applications, such as in semiconductors, vessels, and vehicles. For example, they exhibit high corrosion resistance compared to Sn or Cu alone and have good weldability and ductility [1–4]. In addition, the corrosion resistance of Cu-Sn intermetallic compounds can be controlled and enhanced by increasing the ratio of Sn in the intermetallic compound [1, 2].

Due to these advantages, Cu-Sn intermetallic compound films are often fabricated using solution-based processes, such as electrodeposition and sol-gel [1, 5, 6]. However, the chemical reactions that occur when using the solution-based methods can lead to problems due to the high toxicity of the reactants and difficulty in controlling the chemical reaction due to the complexity of its reagents [7]. In particular, the coating by the electrodeposition method has a limitation in the usage of substrates since the layer must be formed on the conductive electrode. Moreover, the sol-gel method is prone to cause cracks due to the shrinkage of the film when the solvent evaporates [6]. A uniform intermetallic compound phase can be obtained through powder processing, followed by posttreatment at high temperatures, while a long time is required to obtain an intermetallic compound phase. As a result, these fabrication processes raise some disadvantages, such as using a toxic solvent and consumption of heat energy. Moreover, it is very difficult to form a thin intermetallic compound film because the intermetallic compound fabrication process is limited in terms of the shape and size of the final product.

We have developed a kinetic spraying process with the intention of overcoming the problems mentioned above. This dry deposition system uses commercially available powders [8, 9], and its schematics and the principle of the kinetically spraying process are shown in the supplementary section. The surface uniformity is relatively poor compared to the films fabricated via the conventional fabrication methods, like sol-gel, electrodeposition, and sputtering process. However, the kinetically sprayed process does not require high vacuum conditions or posttreatment and the

film can be formed within a very short amount of time. Moreover, previous studies have confirmed that this kinetically spraying process can deposit various types of powder in both thin and thick films [10–14].

Therefore, we have used this kinetically spraying process to deposit a thin film of the intermetallic compound phase through an in situ deposition process at 200°C so that both collision energy between the particles and the substrate, as well as heating substrate, contributed to the formation of the intermetallic compound. Using this kinetically spraying process, we also studied the in situ intermetallic compound formation mechanism. For comparison, we kinetically sprayed films under the following conditions: room temperature deposition using the kinetically sprayed process, in situ deposition at 200°C, room temperature deposition of the Cu-Sn mixture followed by sintering on a hot plate for 3 minutes, and room temperature deposition of the Cu-Sn mixture followed by sintering in a furnace for 1 hour. The sintering step in the furnace was performed at its heating rate of 5°C/min and maintained at 200°C for 1 hour in air atmosphere condition. And then, the sample was allowed to cool to room temperature. Finally, we have demonstrated the possibility of fabricating an intermetallic compound thin film within a short amount of time, showing its application on solder thin films as well as on color-changing thin films.

2. Experimental Details

2.1. Fabrication of Cu-Sn-Based Thin Films. Cu powders (JoinM Co., Ltd., Korea) with an average size of 5 μm and Sn powders (Sigma-Aldrich, USA) with an average size of 10 μm were blended in ethanol at its ratio of 45 wt.% : 55 wt.%. Then, we evaporated the Cu-Sn mixed powder from the ethanol solution using ultrasonication while heat treating at 40°C. Finally, we sieved the mixed powder to obtain an evenly mixed Cu-Sn powder with uniform particle size distribution. We used the kinetically spraying method to deposit the mixed Cu-Sn powder onto the Si wafer. The powder was accelerated to subsonic speed onto the silicon (Si) wafer in a low-vacuum chamber through a macronozzle with its scan rate of 100-150 μm/s so that we could obtain a Cu-Sn thin film with an area of $1 \times 1\,cm^2$. The substrate can be heated to 200°C. In general, the Cu-Sn intermetallic compound shows the solid-state diffusion in the temperature range of 190-220°C [15]. Therefore, we have kinetically sprayed a thin film, followed by sintering at its relatively low annealing temperature of 200°C to form an intermetallic compound in this study. Schematic diagrams of the particle printing system and mechanism are provided in the supplementary section. In order to compare the phase of the film when in situ deposited at 200°C, we have kinetically sprayed the Cu-Sn film at room temperature, followed by sintering on a hot plate at 200°C for 3 minutes, as well as sintering in a furnace at 200°C for 1 hour. We finally evaluated the differences in the phases of these films under these four conditions.

2.2. Evaluation of Cu-Sn-Based Thin Films Fabricated under Different Heating Conditions. As stated in Section 2.1, we have summarized the different heating conditions of the kinetically sprayed Cu-Sn thin films as shown in Table 1. First, X-ray diffraction analysis (XRD) (TTRII; Rigaku, Japan) was used to identify the Cu-Sn intermetallic compound phases obtained under each condition specified in Table 1. Among these samples, we performed energy dispersive X-ray fluorescence (EDXRF) analysis (ARL QUANT'X; Thermo Fisher Scientific, USA) to compare the actual composition ratios of the thin films that were deposited at room temperature to those that were in situ deposited at 200°C as shown in Table 2. In particular, field emission scanning electron microscopy (FE-SEM) (SU-70; Hitachi, Tokyo, Japan) was used to compare the microstructure of the film formed at room temperature vs. in situ deposited at 200°C as shown in Figure 1. Finally, we have used a surface profiler (ET200; Kosaka Laboratory Ltd., Japan) to measure the thickness and average surface roughness of the Cu-Sn composition as shown in Figure 2.

Table 1: Heat treatment condition of the samples fabricated from the Cu-Sn mixed powder.

No.	Deposition condition		Subsequent heating condition	
	Temperature	Time	Temperature	Time
1	Room temperature	3 min	—	—
2	200°C (in situ deposition)	3 min	—	—
3	Room temperature	3 min	Hot plate, 200°C	3 min
4	Room temperature	3 min	Furnace, 200°C	60 min

3. Results and Discussion

First, we performed XRD analysis of the deposited Cu-Sn thin films under various conditions to identify their phases. Figure 3(a) shows the XRD results of the thin films deposited at room temperature vs. those in situ deposited at the substrate temperature of 200°C using a mixed powder of microsized Cu-Sn powder for comparison. As shown in Figure 3, crystalline Cu and Sn peaks are evident in the thin film deposited at room temperature, confirming that the room temperature deposition did not cause any phase transformation as expected [16]. In contrast, the in situ deposition at 200°C successfully formed the Cu_6Sn_5 intermetallic compound phase within just 3 minutes. Additionally, the thin film that was annealed for 3 minutes on the hot plate right after the room temperature deposition contained Cu and Sn peaks only just like the film deposited at room temperature shown in Figure 3(a). Finally, we observed crystalline peaks of Sn and SnO, along with the Cu-Sn intermetallic compound phase of the thin film when the film was deposited at room temperature followed by heat treatment for 1 hour in a furnace, as shown in Figure 3(b). Therefore, it seems that in situ deposition at 200°C for 3 min resulted in the comparable formation of the Cu-Sn intermetallic compound which can be obtained after heat treatment in the furnace for 1 hour. Therefore, we have confirmed that the Cu-Sn intermetallic compound film can be easily manufactured by in situ deposition within a very short time of 3 minutes.

Table 2: The composition of the thin films fabricated from blended Cu-Sn powder based on EDXRF analysis.

No.	Composition of the blending ratio (wt.%)	Annealing condition	Actual composition of the thin film (wt.%)
1	Cu : Sn = 45 : 55	Room temperature deposition for 3 min (without heating process)	Cu : Sn = 31 : 69
2		Heated while depositing on the heated substrate for 3 min (in situ deposition)	Cu : Sn = 36 : 64

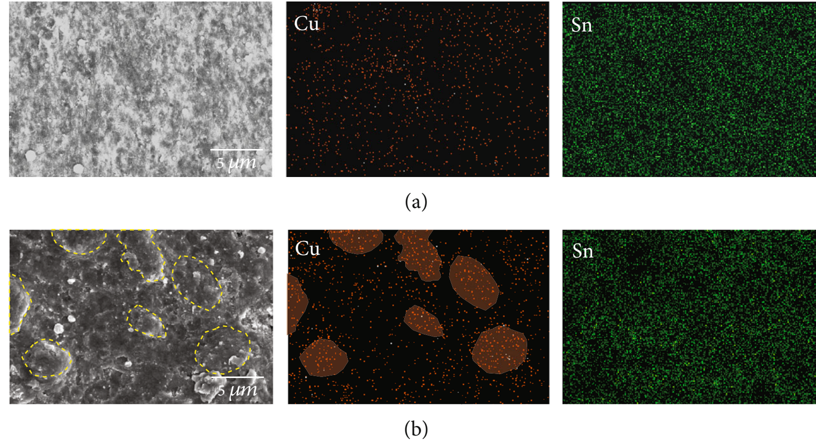

Figure 1: Scanning electron microscopy image of a Cu-Sn-based thin film formed (a) at room temperature and (b) under the substrate heating condition of 200°C, along with elemental mapping results for Cu and Sn. The encircled parts in the image indicate Cu particles.

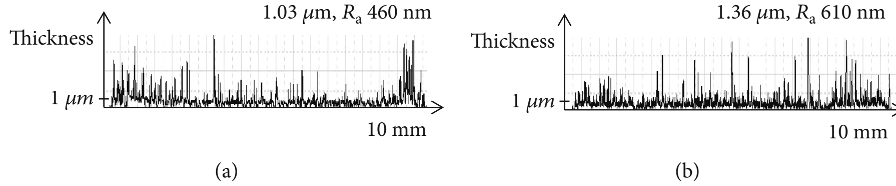

Figure 2: Thickness and roughness of the average surface: the thin film (a) fabricated at room temperature and (b) in situ deposited at 200°C.

And then, we have chosen two types of these thin films which were deposited onto the Si wafer using the mixed powder of microsized Cu particles and Sn particles with its starting composition of 45 : 55 wt.% ratio, both deposited at room temperature and in situ deposited at 200°C. Table 2 shows the actual composition of the deposited film under these 2 conditions, as the actual composition of the film was determined using XRF analysis. As listed in Table 2, for the case of the condition under which the substrate was heated to 200°C, we obtained an actual wt.% ratio of 36 : 64 wt.% for Cu : Sn. This corresponded to the intermetallic compound having a Cu composition 5 wt.% higher compared to the film fabricated at room temperature. Compared to the initial composition, there were 10 wt.% differences in Cu after the deposition. Typically, Sn particles are more likely to cause the plastic deformation on the substrate than Cu particles, as they are readily deposited due to their ductility as well as lower melting point [17]. Therefore, it is comparatively difficult to cause plastic deformation with Cu particles, as Sn particles are more likely to be deposited onto the substrate with plastic deformation than Cu particles. Figure 1 shows SEM images of the Cu-Sn thin films exhibiting different morphologies, depending on room temperature deposition vs. in situ deposition at 200°C.

The elemental mapping analysis results shown in Figure 1 indicate that the Sn and Cu elements were distributed uniformly throughout the sample. However, as shown in Figure 1(b), it appears that the Cu particles (encircled part in Figure 1(b)) maintained their shape after the in situ deposition onto the substrate without causing any deformation since Sn particles acted as a soft matrix in the film, showing plastic deformation. As a result, the surface of the film deposited at 200°C seems to be rough, showing no deformation of Cu. This observation was confirmed by the surface roughness measurement shown in Figure 2. The average surface roughness was measured to be higher for the in situ deposited film at 200°C. Moreover, we can possibly relate these differences in the surface roughness values to its molar volumes. The molar volumes of Cu and Sn were 7 and 16 cm^3/mol, respectively, while the molar volume of the intermetallic compound phase (Cu_6Sn_5) was 118 cm^3/mol [18]. Therefore, the dramatic differences in the molar volume between single

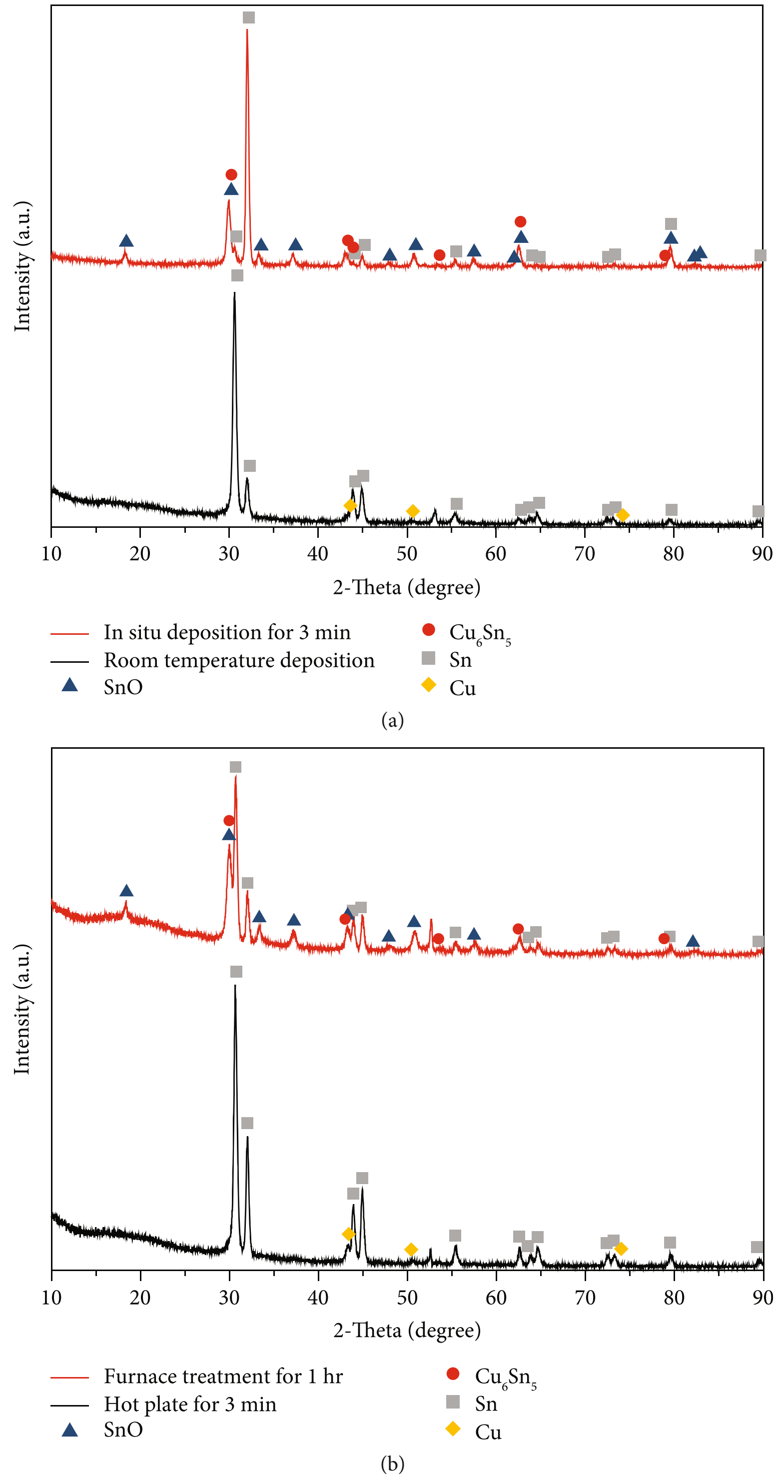

FIGURE 3: The X-ray diffraction analysis results of the Cu-Sn-based thin film: (a) thin films deposited under condition nos. 1 and 2 and (b) heat-treated films under condition nos. 3 and 4.

phases (Cu and Sn) and the intermetallic compound might lead to differences in the surface roughness of the film as well [18, 19].

As shown in Figure 2, the thin films deposited onto the Si substrate under both conditions showed its average thickness to be about 1 μm, while the surface roughness of the in situ deposited film at 200°C was 0.6 μm, which is significantly higher than the roughness of the film with single phases (Cu and Sn) deposited at room temperature.

The fabrication mechanism is summarized in the schematic diagram for the 4 cases as shown in Figure 4. First, the Cu-Sn thin film (Figure 4(a)) was deposited at room temperature; then, we performed in situ deposition of the Cu-Sn mixed powder at 200°C (Figure 4(b)), we heated the

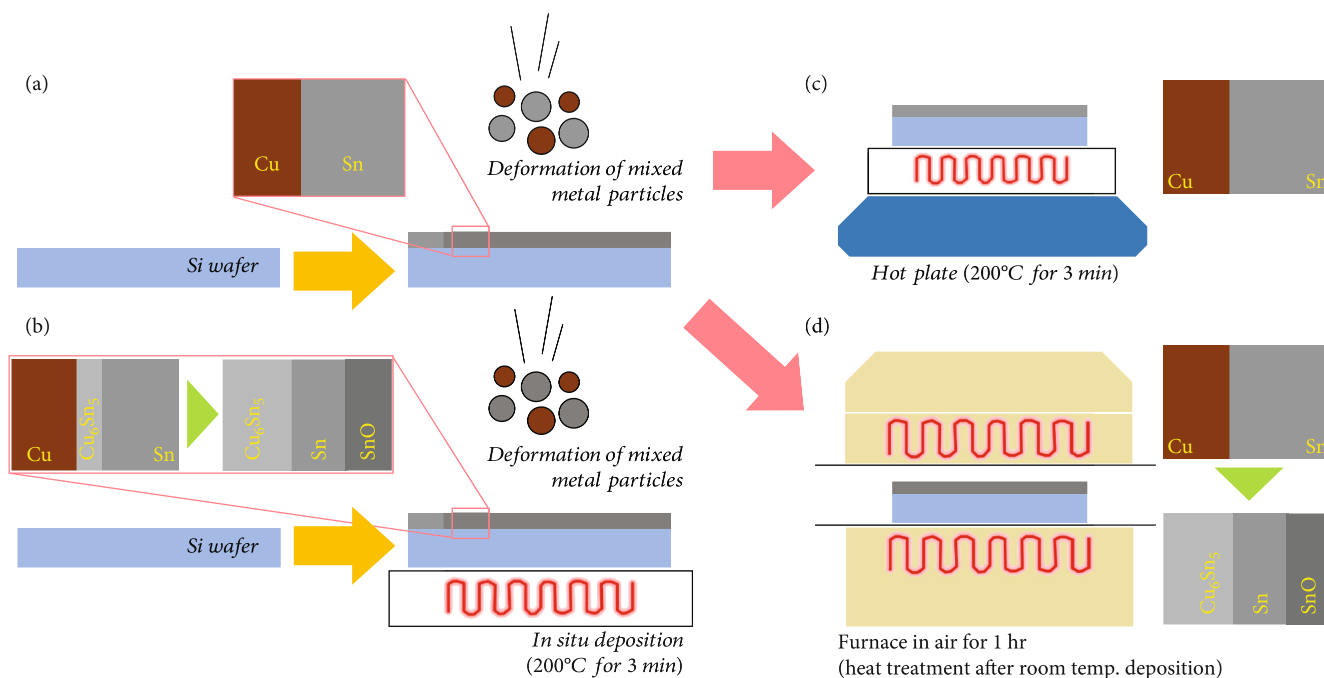

FIGURE 4: Schematic illustration of (a) the Cu-Sn thin film, (b) in situ deposition, (c) heating on the hot plate, and (d) heat treatment in a furnace using a blended powder.

deposited Cu-Sn thin film at room temperature on a hot plate (Figure 4(c)), and finally, we further heated the deposited Cu-Sn thin film at room temperature for 1 hour in a furnace (Figure 4(d)). For the case of the in situ deposition case, the Cu-Sn mixed powder was deposited directly onto the substrate while undergoing heat treatment at its temperature of 200°C. The Sn powder, which has a lower melting temperature than that of the Cu powder, first forms a matrix on the substrate as shown in Figure 1. At the same time, Cu particles were deposited onto the Sn matrix without causing deformation. Additionally, the Cu and Sn powders diffuse, so that the Cu particles enter the Sn matrix via the energy supplied by the heat and collisions. First, the Cu/Sn phase starts to form at the Cu-rich boundary, forming Cu_6Sn_5 at its interface with the Sn-rich boundary as illustrated in Figure 4(b). It seems that the energy supplied by the heat and collisions is sufficient enough to result in the successful formation of an Cu_6Sn_5 intermetallic compound phase within a short time of 3 minutes (Figure 4(b)). The Cu-Sn thin film, which we have kinetically sprayed at room temperature in the form of mixed powders, followed by the posttreatments, such as heating on a hot plate or in a furnace, are shown in Figures 4(c) and 4(d). The thin film that was sintered on a hot plate for 3 minutes did not form any Cu_6Sn_5 phase due to insufficient energy to promote the necessary diffusion at the interface between Cu and Sn. This is possibly due to the fact that we have supplied collision and heat treatment consecutively so that no sufficient energy was provided for phase transformation. However, the Cu_6Sn_5 intermetallic compound phase did form in the thin film when the kinetically sprayed film was heat treated in the furnace for 1 hour, indicating that the diffusion time was sufficient enough to have intermetallic compound formation.

Therefore, we have confirmed that the in situ deposited thin film at 200°C for 3 min successfully formed an intermetallic compound phase of Cu_6Sn_5, indicating that the simultaneous supply of collision and heat energy through heating the substrate at 200°C for 3 minutes is sufficient. The intermetallic compound formed within 3 minutes through in situ deposition showed the same effect as those formed by heating the sample in a furnace at 200°C for 1 hour. This result shows that the kinetically sprayed system is capable of dramatically shortening the phase transformation time as well as having the simplicity of deposition to form intermetallic compounds. This result can open this kinetically spraying process to wide applications for thin intermetallic compound films in free form.

4. Conclusion

We used the kinetically sprayed process to form super-thin intermetallic compound films using a commercially mixed Cu-Sn powder. The in situ deposited thin film with its substrate temperature of 200°C was fabricated to compare its morphologies and to identify phases. As a result, Cu and Sn particles deposited at room temperature were uniformly distributed over the Si substrate, whereas the in situ deposited thin film at 200°C for 3 min showed plastically deformed Sn, which could be used as a matrix for Cu deposition.

We performed XRD analysis to identify the crystalline peaks of the thin films fabricated under the varying heat treatment conditions to find out if the intermetallic compound phase of Cu_6Sn_5 successfully formed in both the in situ deposited film (200°C for a 3-minute process) and the film deposited at room temperature followed by a 1-hour long furnace heat treatment. This result shows that the

simultaneous supply of collision and heat energy was sufficient enough to form a Cu_6Sn_5 intermetallic compound, although it is within a very short time of 3 minutes; this intermetallic compound was evident in the deposited thin film, showing its surface to be 1.33 times rougher than that of the composite film due to its significant differences in molar volume of each phase, such as the Cu, Sn, and Cu-Sn intermetallic phase. Therefore, this kinetically spraying method has demonstrated the possibility of fabricating a thin IMC film within a short amount of time, showing this method to be potentially applicable in solder thin films as well as color-changing films.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest

Acknowledgments

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Supplementary Materials

Figure S1: the schematic of the kinetically sprayed system. *(Supplementary Materials)*

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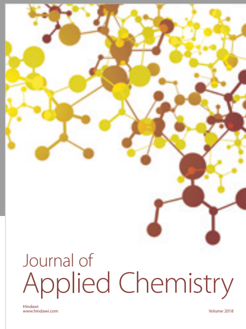
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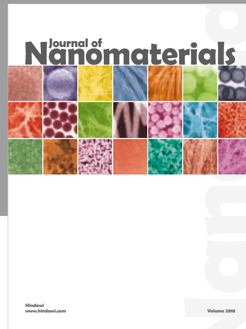
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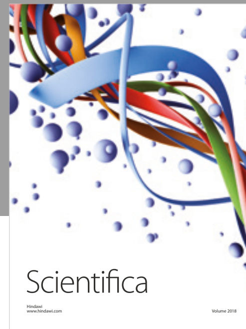
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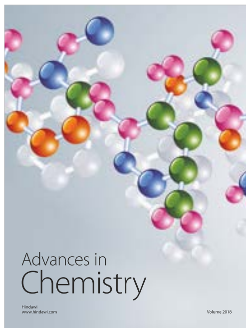
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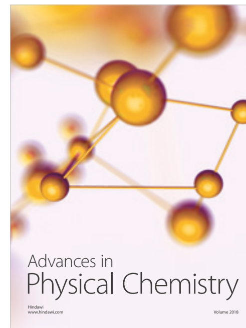
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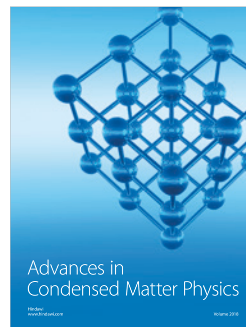
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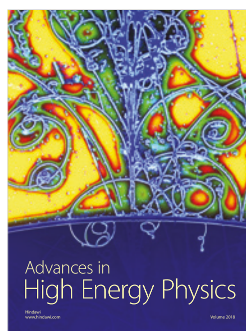
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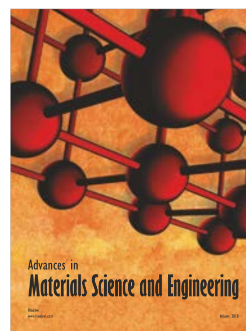
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