Extrinsic Activation Energy for Enhanced Solid-State Metallic Diffusion for Electrical Conductive Ink

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ABSTRACT

In the new area of Advanced Manufacturing Technology, Stretchable Conductive Ink (SCI) has become a future electronic circuit with some unique properties. The Printed Circuit Board (PCB) and other electronic rigid sheet substrate will be shifting into flexible thin layers. SCI will act as interconnect for electronic components. However, the information about diffusion mechanism in SCI is still limited at this time. Therefore, the purpose of this paper is to disseminate information on the role of diffusion mechanism enhance the conductivity in SCI. In addition, this paper introduces the relationship between diffusion mechanism and electron mobilization. Based on this review, the usage of extrinsic energy holds a great potential to enhance the diffusion mechanism in SCI.

Keywords:
Electrons, solid-state, diffusion mechanism, stretchable conductive ink

1. Introduction

Stretchable Conductive Ink (SCI) is defined as an ink which offers electrical conduction. Moreover, it is also had a great expandability which allows many applications and design lightyears ahead of where previously is impossible because of traditional electronics technology [1]. The reliable SCI had low resistivity [2] and the most important is, it allowed the movement of the electron. There are three important components in SCI which are polymer matrix, solvent additive and conductive filler [3]. Polymer matrix act as a binder which holds the particles in the conductive ink. It also gives strength and adhesion to the substrate [4]. The solvent additive usually is a coupling agent. The coupling agent was used in a small quantity and it treat the surface so that the bonding appeared between one surface and another [5]. The filler used in the SCI is the metal base. This is because the filler plays the main role to conducts the electricity.

The previous research had uses silver (Ag) as the filler in the SCI. It is because Ag is excellent electrical and good heat conductor. It has the highest electrical and thermal conductivity compared to any metal. It is also resistance to oxidation [6]. There are several forms of Ag used in previous

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research such as spherical \([7]\), flakes \([8]\) and dendrite \([9]\). The variety shape of the Ag can be seen in Figure 1. The conductive ink with Ag flakes has the higher conductivity compared to conductive ink with Ag spherical. This is because Ag flakes have high surface area contact compared to Ag spherical. The main point here, high surface area contact allowed the electron to move easily from one atom to another atom. The mechanism of atom movement is called diffusion atom.

![Fig. 1. Variety Shape of Ag, (a) Sperical Ag, (b) Flake Ag and (c) Dendrite Ag](image)

Stretchable Conductive Ink (SCI) had attracted a lot of attention for potential application in the manufacturing industry. However, several limitations such as low conductivity, poor stretch ability and high resistance when applied strain has been an issue where limit the commercialization of SCI \([10]\). Therefore, this paper will review previous studies on improvement that have been made to overcome the problem and gather the information about the role of diffusion mechanism to enhance the conductivity in SCI.

2. Reason to Mobilize the Electron

The high resistivity of the SCI has been a barrier to the future innovation for SCI application \([4]\). Therefore, many previous researchers have the focus to solve the problem. One of the methods is by using the Ag nanoparticle size in the conductive ink \([6]\). This research has proved that by using the particle in small size can increase the contact area between the filler in the conductive inks. Another method is by introducing isothermal cure for annealed for nanoparticle metal \([11]\). This research has suggested that the resistivity of the inks is decreasing with film densification and sintering. Moreover, the curing process will reduce the interfacial energy and raise the atomic diffusion mechanism. Surprisingly, the usage of the Ag in dendrite form also can increased the conductivity of the ink because of the branches and trunks of dendritic silvers had rod-shaped with large aspect ratio which can increase the area contact with another dendrite \([9]\). Other than that, there are researcher whom made the comparison between the material to find the best material with great properties to use in the conductive ink. For example, the comparison between the Ag microparticle and Ag nanoparticle in terms of conductivity \([12]\) and the other one is by compared the mechanical and electrical properties between Graphene, Multiwall Carbon Nanotube (MWCNT), Hybrid Graphene and MWCNT. The hybrid conductive ink which composed of Ag nanoparticles and graphene-Ag nanocomposites also has been introduced \([10]\). The small size of Ag Nanoparticles with graphene sheets combine with the large size.

In summary, many studies have focused on what type of material should be used in the SCI, their shape, and their size. Other than that, the suitable polymer matrix and types of the substrate also have been studying. Still, the main point is high contact area between the particles in the SCI will increase the conductivity in the SCI. Thus, it does not matter if we want to use what type of Ag because our main target is to make the electron flow more efficient by reduces the gap between the
particles. That is the reason the enhancement of diffusion mechanism is an important matter to reduces or vanish the gap.

3. Technical of Electron Mobilize

The electron is a negatively subatomic particle which occupied in orbital and moves around the nucleus of an atom. The electron can either be free or bonded to the atom. The free electron usually exists in the metal’s atom because the atom is metallically bonded to each other. Figure 2 shows the metal atom with free electron.

![Fig. 2. Metal atom with free electron](image)

The word free electron is referred to the sea of valence electrons in the metal where they can move freely from one atom to another without being attached to one atom only. The free electron also can be defined as delocalized electron which means the electron can be easily detached from its original atom and move to another atom. The atoms with missing electron will be called metal positive ion. Metal has a unique property which is can conduct the electric because of the sea of the delocalizing electron.

4. Method to Improve the Electron Mobilization

Many previous researchers had focused on diffusion mechanism technique to mobilize the electron. However, none of these researchers had related their study with current intervention. Their research is more on theoretical only.

Diffusion atom is a mechanism of the atom to migrate over another place or replacing its place with another atom. This mechanism can happen in the solid state, liquid state and gasses state [22]. The diffusion in the solid state required the external force to generate the thermal vibration and allow the atom to move. There are two types of diffusion which are self-diffusion and inter-diffusion. The self-diffusion happens only in pure metals. Inter-diffusion occurs in two different of solid material. The example of the type of diffusion can be seen from Figure 3.

![Fig. 3. Type of solid state diffusion process](image)
The mechanism of diffusion can be divided into two categories which are vacancy or substitution mechanism and interstitial mechanism. For substitution mechanism, the diffusion of atom happens when the atom is moving from one atomic site to another site. However, this mechanism occurs only when crystal defects present in the lattice. Interstitial diffusion mechanism is when an atom migrates from one interstitial site to another site without replacing another atom in the crystal lattice. The migrating atoms are relatively small compared to the matrix atom. Figure 4 shows the category of diffusion mechanism. The diffusion mechanism will happen only with the presence of extrinsic force to give thermal vibration to the atom. The extrinsic force can be varied if it can cause the atom to vibrate to generate heat.

![Diffusion Mechanism](image)

**Fig. 4. Categories of diffusion mechanism**

5. Defect in Crystalline

One need only consider the staggering developments in electronics to appreciate the potential of material with reduced dimensions but with same or better than previous one. To make the potential is real, therefore the study on improvement of imperfect lattice should be known. There are many types of the defect presence in the lattice, for example, is interstitials and vacancies. Interstitial diffusion is a mechanism of stranger atom diffuse between host atom in the lattice. Figure 5 shows the illustration of interstitial diffusion.

![Interstitial diffusion](image)

**Fig. 5. Interstitial diffusion**

Table 1 shows on what systems, and under what conditions, is the mobility of vacancies and interstitial are a serious challenge for surface self-diffusion. The motion of atoms in fcc metal is depending on vacancies [13]. There are two categories of vacancies which are monovacancy [14-17] and divacancies [14-18]. The type of the vacancies can be seen in Figure 6 and Figure 7.
Table 1
System and Condition for vacancies and interstitial

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>Vacancy</th>
<th>Interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Systems to mobilize for surface self-diffusion</td>
<td>The neighbour atom will carry the energy and let the atom to move. The mechanism easily achieves when the atoms vibrate strongly, which mean in high temperature</td>
<td>Low activation energy process, however interstitial diffusion features high diffusion coefficient (For example gold element in silicon)</td>
</tr>
<tr>
<td>2</td>
<td>Condition to mobilize for surface self-diffusion</td>
<td>The vacancy is a condition when the atom is missing from the lattice.</td>
<td>Interstitial is a condition when an extra atom occupies in a normal unoccupied site</td>
</tr>
</tbody>
</table>

The vacancy concentration affecting the concentration diffusivity of concentration. The diffusivity of vacancies depends on two regimes of temperature [19]. The two regimes of temperature are

i. Low-Temperature Extrinsic Regime

ii. High-Temperature Intrinsic Regime

Low-temperature extrinsic regime happens where the vacancy concentration is independent of temperature and is determined by solute concentration. There are two contributions for extrinsic for electron mobility which are lattice and the impurities. For lattice factor, the high temperature allowed the atom to vibrate faster which cause the atom to vibrate and impeded the electron movement. The result from this condition will increase the resistance of the material which decreases the conductivity. Meanwhile for impurity factor, if there is another element in the host lattice, it is also will impede the movement of the electron when the impurity pushes out the electron to the host lattice because of the difference electronegativity. This situation will increase the resistance in material and decrease the conductivity. The illustration for both factors can be seen in Figure 8 and Figure 9.
The high-temperature Intrinsic regime is where the vacancy concentration is dominated by intrinsic thermally degenerated vacancies. Intrinsic semiconductor [20] is a pure semiconductor which the element tends to bond to each other with covalent. For example, for Silicon which had four electrons on the outer layers are tended to bond with another atom by a covalent bond. The free electron only exists in natural causes which are, when the high temperature had exposed to the lattice. The high temperature causes the bond break and decreases the resistance. The illustration of the intrinsic regime can be seen in Figure 10.

6. Future Focus

The printed electronics is a promising tool to create an innovative and unique product in the future. By shifting the Printed Circuit Board (PCB) and rigid sheet to flexible layers can broaden the invention and application of the product. However, the reliability of the printed electronics is depending on the availability of the nanotechnology-based functional inks. Therefore, the credibility and dysfunctionality of the nanotechnology-based functional inks are now being studied. Moreover,
the high sales of silver nanoparticle-based ink have been the example of successful to commercialize the nanotechnology.

The formulation of the nanostructure with Ag based has led to a huge range of application. Nevertheless, it is important to find a way to improve the availability of the nanostructure ink with Ag based. Previous research had used thermal sources for curing process [11] and to sintering the behaviour of material [21]. This method has suggested can improve the behaviour of the material by control the imperfections in the lattice structure of material. Unfortunately, the Ag-based ink still cannot be commercialized into large application due to it can only withstand with small amount of voltage. Hence, more research should be made to find the best method to improve the functionality of the Ag-based ink.

A successful outcome of these efforts will increase the application field of nanotechnology Ag-based ink.

7. Conclusions

In summary, the diffusion can increase the conductivity in the SCI. The diffusion mechanism can reduce the crystalline defect in the crystallography. Although there is no clear evidence that the diffusion mechanism can increase the conductivity in the SCI, in theoretically the method was proven. Therefore, the experiment should be done to prove the theory. Meanwhile, the intrinsic and extrinsic temperature hold the great potential to activate and mobilize the diffusion mechanism.

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