Electroless Bismuth Plating as a Peripheral Technology for SiC Power Devices

Ei Uchida^{1*}, Kaoru Tanaka¹, Miri Okada², Takaaki Tsuruoka², Kensuke Akamatsu² and Hidemi Nawafune²

1. Ishihara Chemical Co., Ltd. 5-26 Nishiyaniwara-cho, Hyogo-ku, Kobe, Hyogo-ken 652-0806 Japan

2. Frontiers of Innovative Research in Science and Technology (FIRST), Konan University, 7-1-20 Minatojima-minami, Chuo-ku, Kobe, Hyogo-ken 650-0047 Japan

*Corresponding author: Fax: +81-78-682-4513, and e-mail: uchida-e@unicon.co.jp

Bismuth plated films have been used as a high-temperature joining in SiC power device because of their outstanding melting point. Electroless bismuth plating intended to have a “weak acidic” was investigated using Sn^{2+} ion as the reducing agent and citrate as the complexing agent. Complex baths exhibited good stability, and pure bismuth films were deposited. Experiments in polarization characteristics confirmed the mixed potential theory including local potential-current relationships for bismuth deposition.

Key words: Electroless Bismuth Plating, Redox System of Sn Ions, Mixed Potential Theory, SiC Power Device

1. INTRODUCTION

Silicon (Si) semiconductors are used for almost all electronic devices, including diodes, transistors, integrated circuits (ICs), large-scale integrated circuits (LSIs), ultralarge-scale integrated circuits (ULSIs), photodiodes, and solar cells. In particular, although Si semiconductors have been widely used for the power converters that convert DC to AC or AC to DC on the input and output respectively, they are limited (Si-limitations) in terms of miniaturization and power conversion efficiency. Therefore, a semiconductor device capable of exceeding these Si limits is desired^[1].

A silicon carbide (SiC) power semiconductor, which has attracted attention from the above standpoint, permits a variable-speed drive for the conversion of high-voltage and high-current power, so it doesn't require multiple transformers. Therefore, SiC power semiconductors allow fewer semiconductor devices to be connected in series. This also enables high-speed switching of the inverter, allowing a smaller passive device in the rectification section, and consequently, a smaller size and higher density for the entire system. Moreover, because of their high heat resistance, SiC power semiconductors also allow a power converter to be installed in high-temperature usage environments, such as those for hybrid electric vehicles (HEVs)^[2]. Therefore, using SiC power devices enables considerable energy savings due to their superior current conversion efficiency, and allows the conversion of high-voltage, high-current power. Accordingly, it is expected that such a device will be used for electric vehicles, solar power generation, inverter control of various industrial equipment, and saving power and reducing the size of the power supply in information-processing equipment, for example. In addition, because of their high heat resistance, SiC power devices can be used at high temperatures. Therefore, they require different peripheral technologies than those in existing Si devices.

To mount an existing Si device on a circuit board, alloy plating using tin with 3% bismuth (melting point:

225°C), tin with 3.5% silver (melting point: 221°C), or tin with 0.7% copper (melting point: 227°C) depending on the application, has conventionally been used, and tin plating (melting point: 232°C) has started to be used for chip parts. However, for mounting parts on SiC power devices and power LEDs, etc., which are used in high-temperature environments (200–250°C), such as near HEV engines, the development of high-temperature lead-free plating for bonding has been desired. Existing lead-free solder plating film is used to bond Si devices at low melting points. On the other hand, the existing high-temperature lead solder (Sn-85wt%Pb) used for high-temperature bonding is limited in use: although its use is not restricted currently under RoHS, it may be restricted in the future after a review of RoHS substances. Environmental considerations are another reason why usage of the above solder is limited. The Sn-80wt%Sn alloy also has problems such as its cost as well as embrittlement, which results from the formation of intermetallic compounds. For these reasons, Sn-Zn, Sn-Cu-Zn, and Sn-Fe-Zn alloy plating with a melting point of 250°C or higher, and bismuth plating are appropriate for mounting parts on SiC power devices and power LEDs, etc. Regarding tin alloys, zinc is a promising alloy constituent in terms of its melting point. However, zinc's solubility limit is extremely low in tin. This raises concerns about the possibility of property degradation due to zinc oxidation (standard electrode potential: -0.763 V). Accordingly, Sn-Cu-Zn and Sn-Fe-Zn alloy plating, which stabilize zinc using copper and iron, respectively, are considered to be promising. On the other hand, the melting point of bismuth is 271.3°C, and bismuth electroplating has been put to some practical use.

For circuit boards with electrically isolated areas, the formation of a bonding film through electroless plating, in particular, autocatalytic electroless plating, which doesn't cause the elution of copper from wiring is desired. In the first half of the 1990s, Senda et al. undertook intensive studies for electroless plating of group 12–16 metals in the periodic table. They reported

that electroless plating with lead, antimony, indium, and cadmium using titanium trichloride as the reducing agent is possible^{[1]-[4]}, but electroless plating with bismuth is difficult^{[5],[6]}. Electroless bismuth plating using tin chloride (II) as the reducing agent is reported to be possible^[7]. However, the appropriate pH range is extremely limited in the alkaline range, and while deposition does not occur at a pH of 8.3 or below, bath decomposition does occur at a pH of 9.0 or higher. They did not study the electrochemical mechanism of deposition^[7].

Based on the report from Senda et al.^[7], this study establishes the bath composition and plating conditions regarding autocatalytic electroless bismuth plating in a weakly acidic citric acid complex bath using a Sn^{2+} ion as the reducing agent. The subjects are electronic components as the composite materials of alkali-developable resists, etc., which have a problem with alkaline resistance. The study also discusses the deposition mechanism from an electrochemical point of view.

2. EXPERIMENTAL

2.1 The influence of bath composition factors on deposition rate and bath stability

Table I shows the basic bath composition and plating conditions. Electroless bismuth plating bath, using tin chloride (II) as the reducing agent, that is referred to the composition reported by Senda et al.^[7]. Tin sulfate (II) and bismuth nitrate (III) were used as the reducing agent and the bismuth salt, respectively. Citric salt was chosen as the main complex agent because the citric acid (cit) complex formation constants of Sn^{2+} and Bi^{3+} ions are $\log K_1 = 15.4$ ^[8] and $\log \beta_2 = 14 - 18$ ^[9] for Sn^{2+} -cit and Bi^{3+} -cit, respectively.

A rolled copper sheet (20×20×0.3 mm), which was electrolytically degreased with alkaline, was treated with acid (10% sulfuric acid) and then immersed in a palladium chloride/hydrochloric acid solution (Pd concentration 1,000 mg L⁻¹, 0.1 mol L⁻¹ hydrochloric acid) for palladium displacement. Then it was immersed in a plating bath (liquid volume: 100 mL, bath temperature: 60 °C) for 1 hour. The deposition rate was calculated from mass change after the plating. The stability of the plating bath was evaluated by the bath conditions after the plating.

2.2 The surface morphology, melting characteristics, and crystal structure of the deposition film

The surface morphology and crystal structure of the deposition film were evaluated using a scanning electron microscope (JSM-5200 from JEOL; hereinafter, the "SEM") and an X-ray diffraction system (Ultima IV from Rigaku; hereinafter, the "XRD"). The melting point of the deposition film was evaluated using thermal analysis equipment (Thermoplus Evo DSC8230 from Rigaku).

2.3 Local polarization curves

To clarify the deposition mechanism of the electroless bismuth plating in this study, the local polarization curves were measured using the potential sweep method. The measuring equipment used for this was the HZ-5000 electrochemical measurement system from Hokuto

Denko, and the potential sweep rate was set at 10 mV s⁻¹. The working electrode was a 2.2 mm in diameter platinum disk electrode implanted in a Teflon holder, which was plated with approximately 3 μm-thick electric bismuth at a cathode current density of 10 mA cm⁻² each time measurements were made. A platinum needle was used as the counter electrode, and a silver/silver chloride electrode (3.3 mol L⁻¹ KCl) was used as the reference electrode. All potentials in this article were referred to the reference electrode. The solution used to measure the local anodic polarization curve was the basic bath shown in Table I, excluding bismuth nitrate (III). The solution used to measure the local cathodic polarization curve was the basic bath, excluding tin sulfate (II). Dissolved oxygen was eliminated from the solutions used for these measurements by aerating them with nitrogen gas for 10 minutes beforehand.

Table I Basic bath composition and plating condition for electroless Bi plating.

Bismuth (III) methanesulfonate (mol L ⁻¹)	0.08
SnSO ₄ (mol L ⁻¹)	0.04
Na ₃ citrate (mol L ⁻¹)	0.34
Nitrilotriacetic acid [NTA](mol L ⁻¹)	0.2
NaCl (mol L ⁻¹)	0.2
pH (adjusted with 10% H ₂ SO ₄)	3.0
Temperature (°C)	60

3. RESULTS AND DISCUSSION

3.1 The influence of bath composition factors on deposition rate and bath stability

Bismuth deposition rate was measured by individually changing the bath composition factors under the basic plating bath composition and plating conditions shown in Table I. The results are shown in Figure 1. All of the bath composition factors shown in Figure 1 significantly influenced bismuth deposition rate. With tin sulfate (II), the maximum deposition rate was close to 0.04 mol L⁻¹, while this rate was extremely slow at low concentrations. NTA was added as the auxiliary complex agent. When it was not added, a white precipitate formed and bismuth deposition was not observed. When it was added, a white precipitate did not form and the deposition rate reached a maximum at a concentration of 0.1 mol L⁻¹. Bismuth deposition rate was reduced with increase of NTA concentration. In the bath without sodium chloride, bismuth deposition was not observed. The bismuth deposition rate was 3–4 mg cm⁻¹ h⁻¹ (3–4 μm h⁻¹) when the sodium chloride concentration was 0.1–0.3 mol L⁻¹. Regarding the impact of chloride ions on the rate of bismuth deposition, they do not contribute to complex formation. They may contribute to the absorption of Sn^{2+} ions as the reducing agent for the electrode surface, but the details are unknown and need to be examined.

The pH and bath temperature greatly influence the bismuth deposition rate. This rate was increased with decrease of the pH. At pH 2 and pH 8, however, bath decomposition occurred and a deposition of bismuth powder was observed in the bath. Regarding the bath

Fig. 1 Effects of bath components and plating conditions on deposition rate.
Solid symbol: bath decomposition

temperature, the deposition rate was low at 40–50°C, with a value of 4 mg cm⁻¹ h⁻¹ (4 μm h⁻¹) at 60–70°C.

Based on the above results, the basic bath composition and plating conditions shown in Table I were chosen. Figure 2 shows the relationship between the plating time and the amount of bismuth deposition (average thickness of the bismuth film), which was examined by conducting continuous plating over a long time under the basic plating bath composition (liquid volume: 500 mL) and plating conditions. The plating film increased in an almost linear fashion as the plating time increased, and bath decomposition was not observed. In addition, bismuth deposition did not take place at all on a rolled copper sheet for which palladium displacement was not done. These facts suggest that autocatalytic bismuth deposition was taking place.

3.2 The surface morphology, melting characteristics, and crystal structure of the deposition film

Figure 3, Figure 4, and Figure 5, respectively, show the surface morphology, crystal structure, and melting characteristics of the deposited bismuth film (thickness:

Fig.2 Relationship between amount of deposits and plating time.

approximately 5 μm) on a rolled copper sheet displaced by palladium under the basic bath composition and plating conditions shown in Table I. The surface

morphology of the deposition film was relatively flat, smooth, and dense.

It was revealed that highly crystallized bismuth oriented to the low index plane was deposited. The DSC curve shown in Figure 5 is the result of measuring the film deposited on the rolled copper sheet displaced by palladium. The melting point of the deposited bismuth was 273.0°C. This was close to the literature value, which is 271.3°C. A minor peak near 250°C was attributed to the eutectic point (250°C) of Bi-Bi₂Pd, which was the eutectic alloy of palladium deposited on the copper sheet as the results of displacement treatment [10].

From the results described above, it is suggested that the deposited film is bismuth and there was no co-deposition of tin compound as the reducing agent or tin as the reductant from its bath composition and standard electrode potential.

3.3 Deposition mechanism

Generally, the deposition mechanism of autocatalytic electroless plating is interpreted based on mixed potential theory [11]. In relation to this, the local anodic and cathodic polarization curve of the electroless bismuth plating as the subject of this study were measured by applying the potential sweep method, to validate the mixed potential theory. Figure 6 shows the results of the measurement of the local polarization curves for the basic bath composition and plating conditions shown in Table I. The solution used to measure the local anodic polarization curve was the basic bath composition shown in Table I, excluding bismuth nitrate (III), which is bismuth salt. The solution used to measure the local cathodic polarization curve was the basic bath composition shown in Table I, excluding tin sulfate (II), which is the reducing agent.

Curve a is the local anodic polarization curve concerning the same solution as the basic bath composition, excluding bismuth nitrate (III), and the anode current flows at a potential that is higher than the natural electrode potential, near -0.22 V. It is believed that the anode current, which shows a peak near 0.1 V, can be attributed to the oxidizing reaction of the Sn²⁺ ion, while the anode current at a potential that is higher than the small current peak near 0.3 V can be attributed to the dissolution reaction of bismuth. On the other hand, curve b is the local cathodic polarization curve concerning the same solution as the basic bath composition excluding tin sulfate (II), and the cathode current flows at a potential that is lower than around -0.17 V as the natural electrode potential. The polarization resistance of the reduction reaction of Bi³⁺ ion is small, and the plateau region at a potential that is lower than -0.5 V is the limiting current of bismuth deposition. The mixed potential calculated from local polarization curves a and b is -0.173 V, and this mixed potential is almost identical to the natural electrode potential of the bismuth electrode in the basic bath.

A magnified view of the area around the mixed potential is shown in Figure 7. The value of the current at the mixed potential, which determines the deposition rate of the electroless bismuth plating, is 0.12 mA, and the surface area of the working electrode is 0.038 cm².

Accordingly, the current density is 3.16 mA cm⁻² and

the bismuth deposition rate obtained from this current density is 8.2 mg cm⁻² h⁻¹. This is approximately twice as high as the actual measured value of the deposition rate of the electroless bismuth plating shown in Figure 2, which is 4.0 mg cm⁻² h⁻¹. The use efficiency of the reducing agent for bismuth deposition in electroless bismuth plating is approximately 50%, and the remaining approximately 50% appeared to have been consumed in the reduction of the dissolved oxygen, etc. Accordingly, it is concluded that the mixed potential theory is basically valid for the subject bath system.

Fig. 3 Surface SEM image at the obtained deposit (thickness 10 mm).

Fig. 4 XRD pattern of the obtained deposit.

Fig. 5 DSC curve of the obtained deposit.

Fig. 6 Polarization curves of Bi electrode at 60°C.

Fig. 7 Polarization curves near mixed potential of Bi electrode at 60°C.

plating bath. Accordingly, it is concluded that the mixed potential theory is basically valid for the subject electroless bismuth plating.

REFERENCES

- [1] A. Senda, T. Nakagawa, Y. Takano, and T. Kasanami, *Hyomen Gijutsu*, **43**, 324-9 (1992).
- [2] A. Senda, T. Nakagawa, and Y. Takano, *Hyomen Gijutsu*, **43**, 589-94 (1992).
- [3] A. Senda, T. Nakagawa, and Y. Takano, *Hyomen Gijutsu*, **43**, 694-9 (1992).
- [4] A. Senda, T. Nakagawa, and Y. Takano, *Hyomen Gijutsu*, **43**, 967-72 (1992).
- [5] Y. Suzuoka, A. Ohki, T. Mizutani, and M. Ieda, *J. Phys. D. Appl. Phys.*, **20**, 511-7 (1987).
- [6] L. F. Lou, *J. Appl. Phys.*, **50**, 555-4 (1979).
- [7] A. Senda, T. Nakagawa, and Y. Takano, *Hyomen Gijutsu*, **44**, 145-50 (1993).
- [8] A. Survila, Z. Mockus, and S. Kanapeckaite, *Electrochimica Acta*, **46**, 571-7 (2000).
- [9] L. Sillén and A. Martell, "Stability Constants of Metal-Ion Complexes, Special Publication", The Chemical Society, London, No.17, (1964) p. 478.
- [10] R. Elliott, "Constitution of Binary Alloys, First Supplement", McGraw-Hill (1985) p.188.
- [11] M. F. Paunovic, *Plating*, **55**, 1161 (1968).

(Received September 30, 2013; Accepted February 13, 2014)

4. CONCLUSION

This study established the bath composition and plating conditions concerning autocatalytic electroless bismuth plating from a weakly acidic citric acid complex bath using Sn^{2+} ions as the reducing agent, and the subjects were the electronic components as the composite materials of alkali-developable resists, etc. At the same time, local polarization curves were measured in this study to electrochemically analyze the deposition mechanism. The following conclusions were derived from the results and discussion.

Electroless bismuth plating from a weakly acidic citric acid complex bath using Sn^{2+} ions as the reducing agent is possible, and bismuth film was deposited autocatalytically on a copper sheet which displaced palladium. Superior bath stability was demonstrated under basic bath composition and plating conditions, and extraneous deposition of bismuth on the beaker wall, etc. was not observed. The deposited bismuth film was relatively flat, smooth, and dense, and its melting point was found to be 273°C. Mixed potential was seen in the local polarization curves in the basic plating bath system, and this potential was almost identical to the natural electrode potential of the bismuth electrode in the