

Improvement in flip-chip bonding by reduction of oxides using hydrogen radicals

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Abstract

The demand for high-density mounting increased because of the miniaturizing of a variety of electronic equipment such as personal computers and cellular phones. In response, the use of packaging methods such as flip-chip bonding has also increased to meet this demand. However, during the soldering process, the presence of oxides on the solder bump surface can obstruct the interconnections because oxides with a high melting point do not melt during the process. Methods for removing oxides from the solder bump surface have been developed. In this paper, we propose a novel oxide reduction method for the solder bump surface. This method uses hydrogen radicals generated by a heated catalyzer consisting of a tungsten wire. We have successfully demonstrated that the removal of oxides from the solder bump surface is possible by this treatment. Furthermore, we have verified that this method is effective in improving the reliability of flip-chip bonding without flux.

Key words: Solder bump, Flip-chip bonding, Hydrogen radical, Hot-wire method

1. Introduction

Recently, as various electronic equipment, such as portable telephones, digital cameras, and personal computers, have been miniaturized and made multi-functional. This has been achieved through the use of high-density packaging technology including area-array-type packages, flip-chip bonding, ball-grid-arrays (BGAs), and chip-scale packages (CSPs). These packages have solder bumps on the electrodes. The solder bumps are used for joining the package to a substrate. The connection is established by melting the solder. Therefore, during the soldering process, if there are oxides present on the solder bump surface, then they would obstruct the interconnections as oxides with a high melting point do not melt during soldering. Various oxide removal methods have been proposed. The existing oxide removal methods are the flux method and the plasma method [1]. Both these methods have their disadvantages. The flux method affects the environment and the equipment because it uses organic solvents [2]. In addition, the flux residue causes an impedance anomaly. The plasma method, which does not use flux, is not cost-effective because the plasma supply equipment is expensive; moreover, the substrate is damaged by the plasma.

In this paper, in order to resolve the problems

arising from the use of existing oxide removal methods, we propose a novel oxide removal method that uses the hydrogen radicals produced on a heated tungsten wire (hot-wire). We have successfully demonstrated that the removal of oxides from the solder bump surface is possible by this treatment. Furthermore, we have verified that this method is effective in improving flip-chip bonding without the use of flux.

2. Experimental

The method proposed in the present study is called the hot-wire (HW) method; it is applied to the removal of various metallic oxides [3], removal of contaminants from extreme ultraviolet (EUV) mirrors [4], and ink-jet printing technology [5]. Figure 1 shows the schematic representation of the HW apparatus, which was used for the generation of hydrogen radicals. H₂ gas was used as the source gas. The solder bump and the Sn substrate were installed in a vacuum chamber having a pressure of less than 5.0×10^{-5} Torr. A tungsten (W) wire with a diameter of 0.5 mm and length of 800 mm was used as the catalyst. It was kept parallel to a substrate holder at a distance of 50 mm. The temperature of the tungsten wire, which was monitored by an infrared spectrometer, was changed from 1400 to

1700 °C. The temperature of the substrate holder was measured using a thermocouple. This technique was also used for the generation of high-density radicals. In particular, hydrogen radicals with a radical density of more than 10^{14} cm^{-3} could be easily produced by the catalytic cracking of hydrogen molecules with a heated tungsten catalyzer, although the generation of such high-density hydrogen radicals was not easy when the conventional plasma-enhanced CVD (PECVD) process was used [6].

The Sn substrate (10 mm × 10 mm) was folded on the sample holder. Then, the oxide on the Sn substrate surface was removed by using the hydrogen radicals. The flow rate of H_2 was maintained at 50 and 100 sccm ($1 \text{ sccm} = 6.9 \times 10^{-7} \text{ mol s}^{-1}$) by using a mass flow controller. The cleaning conditions are summarized in Table I. After this treatment, the surface conditions of the Sn substrate were characterized by ex-situ x-ray photoelectron spectroscopy (XPS) measurements using monochromatic $\text{MgK}\alpha$ radiation with emission angles of 90° .

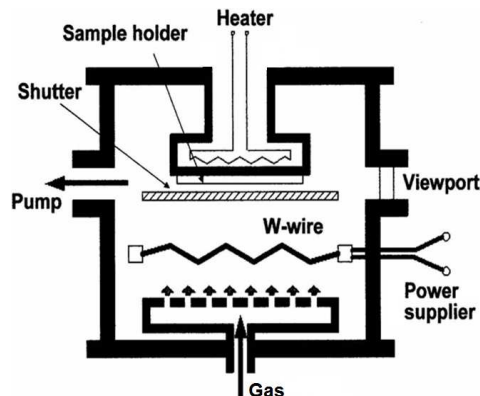


Fig.1. Schematic diagram of HW apparatus.

Table I Cleaning conditions

Source gas	$\text{H}_2, \text{NH}_3, \text{N}_2:\text{H}_2$ = (96:4)
Flow rate (sccm)	50, 100
HW temperature (°C)	1400, 1500, 1600, 1700
Maximum sample temperature (°C)	90
Treatment time (min)	1

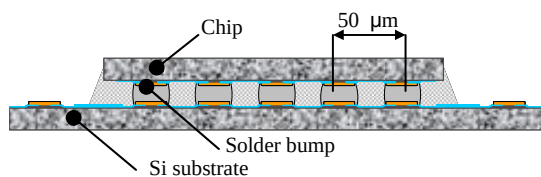


Fig.2. Schematic cross section diagram solder bump.

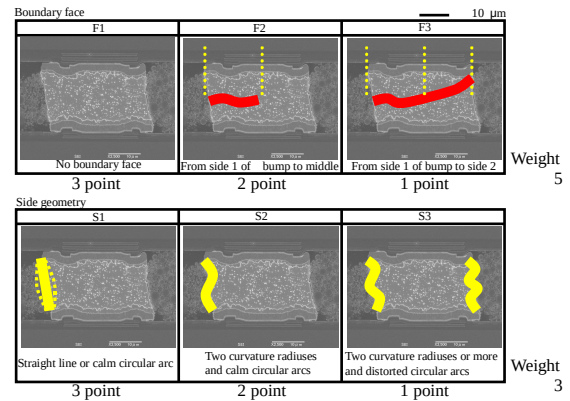


Fig.3. SEM image of the cross section of the flip-chip bonding.

3. Results and discussion

3.1. Effect of hydrogen radical treatment on flip-chip bonding

The solder bump (Sn-Ag) on the chip (3 mm × 3 mm) was 30 μm in diameter and 50 μm in pitch, as shown in Figure 2. Using 100% hydrogen gas as the source gas, we could generate the hydrogen radicals and remove the oxide on the solder bump surface using these radicals. Then, the solder bumps were reflowed without flux in the atmosphere, and the bonding condition was observed by using a scanning electron microscope (SEM). The SEM image of the cross section of the flip-chip bonding is shown in Figure 3. As shown in Figure 3, these points were applied to the connection state of an interface and a side surface in a solder joint, and 44 connections per one tip were evaluated by the product of these points ($3 \text{ point} \times 5 \times 3 \text{ point} \times 3 = \text{maximum points } 135$).

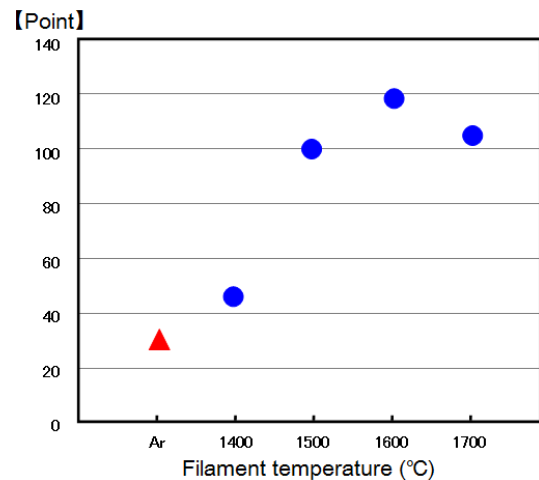


Fig.4. Average point vs. filament temperature.

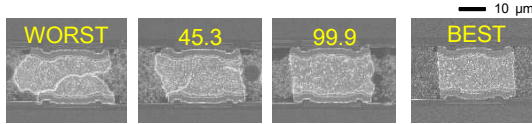


Fig.5. SEM cross section photograph of the best connection state, the worst connection state and the average connection state after hydrogen radical treatment at the filament temperature of 1400 °C and 1500 °C.

The weight of the interface is more important than the weight of the side surface because it is believed that the connection state of the oxide remarkably influence the interfacial connection state. These points were applied to the connection state by this evaluation standard, and the average point was calculated. Moreover, the sample in the Ar plasma treatment for 1 min was evaluated as a comparison object for the HW treatment. Figure 4 shows the result. It can be verified that the proposed method is more effective in improving the flip-chip bonding by the hydrogen radical treatment than the Ar plasma treatment, which is the conventional method. For this reason, it is speculated that the oxide removal ability of the HW treatment is superior to that of the Ar plasma treatment. Figure 5 shows the SEM section photograph of the best connection state, the worst connection state, and the average connection state after the hydrogen radical treatment at a filament temperature of 1400 °C and 1500 °C. Therefore, it is clear that the hydrogen radical treatment for 1 min at a filament temperature of 1500 °C or more is effective in improving the flip-chip connection state.

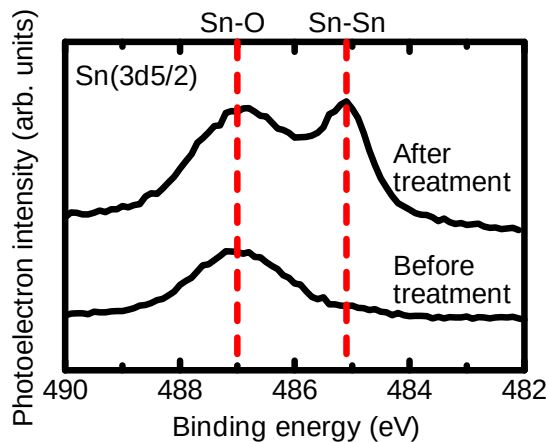


Fig.6. Sn (3d5/2) XPS spectrum before and after 1-min hydrogen radical treatment.

3.2. Effect of hydrogen radical treatment on the oxide removal

Figure 6 shows the Sn (3d5/2) XPS spectrum before and after the 1-min hydrogen radical treatment at various filament temperatures. The peak due to the Sn–O bonds is observed before the treatment. After this treatment, the value of the Sn–O (487 eV) peak decreased in the case of every filament temperature, and simultaneously, the value of the Sn–Sn (485 eV) peak increased. These results imply that hydrogen radicals reduced the oxide layer on the Sn surface, at least near the surface. The thickness of the oxide layer was calculated from the ration of the Sn–O bonds to that of the Sn–Sn bonds, according to the following equation.

$$d = \lambda_o \sin \theta \ln \left[\left(\frac{\sigma_{Sn} M_{Sn} \lambda_{Sn}}{\sigma_o M_o \lambda_o} \right) \frac{I_o}{I_{Sn}} + 1 \right] \quad (1)$$

In this equation, d is the thickness of the oxide layer, λ_{Sn} is the photoelectron escape depth for Sn, λ_o is the photoelectron escape depth for the Sn oxide, θ is the photoelectron take-off angle, δ_{Sn} is the photoelectron cross section of Sn, δ_o is the photoelectron cross section of the Sn oxide, M_{Sn} is the molecular weight of Sn, M_o is the molecular weight of the Sn oxide, I_S is the photoelectron intensity of Sn, and I_o is the photoelectron intensity from Sn oxide. The following values were used for the calculation; $\lambda_{Sn} = 1.87$ nm, $\lambda_o = 2.20$ nm, $\theta = 90^\circ$, $\delta_{Sn} \cong \delta_o$, $M_{Sn} = 118.7$, $M_o = 150.7$.

The thickness of the Sn oxide layer at various filament temperatures is summarized in Figure 7. Before this treatment, the thickness of the Sn oxide layer was approximately 6 nm. With respect to the filament temperature, when H_2 or NH_3 was used as the source gas, the thickness of the oxide layer at the filament temperature of 1500 °C or more was less than 1.5 nm.

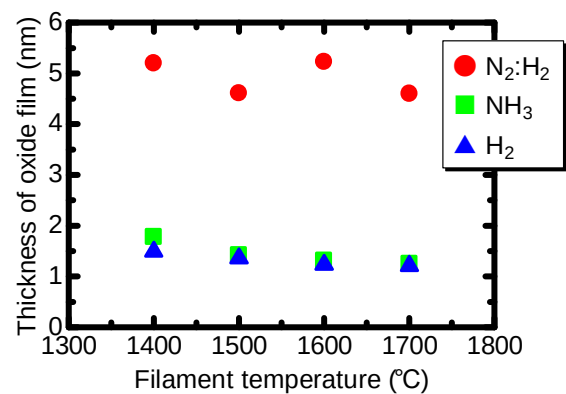


Fig.7. Thickness of oxide film vs. filament temperature.

However, the thickness of the oxide layer did not decrease and was saturated to a certain value, although the temperature of the filament was increased further. It is believed that this saturation was because a natural oxide layer was formed on the surface of the Sn substrate. The surface condition of the Sn substrate was measured by ex-situ XPS, although the oxide on the Sn substrate could be removed by the proposed treatment for 1 min at a filament temperature of 1500 °C. With respect to source gases, the effect of the oxide removal of H₂ and NH₃ was similar. Hence, we can consider that the oxide was mainly removed by hydrogen radicals. However, only about 1 nm of the oxide was removed by using the forming gas at any HW temperature. It is considered that hydrogen radicals are not sufficient for the complete oxide removal because the hydrogen content is only 4%. As a result, it is suggested that the proposed method is effective in improving the flip-chip bonding without flux when the oxide thickness is 1.5 nm or less. Therefore, the hydrogen radical treatment for 1 min is not sufficient for the improving the flip-chip bonding by using the forming gas.

The temperature of the filament was fixed to 1600 °C by using the forming gas as the source gas. The treatment time dependence of the thickness of the oxide film is shown in Figure 8. It can be confirmed that the thickness of the oxide film becomes 1.5 nm or less when the treatment time is 15 min or more. Moreover, the thickness of the oxide film is saturated to a constant value. When the forming gas is used as the source gas, it can be suggested that the hydrogen radical treatment for 15 min or more is effective in improving the flip-chip bonding.

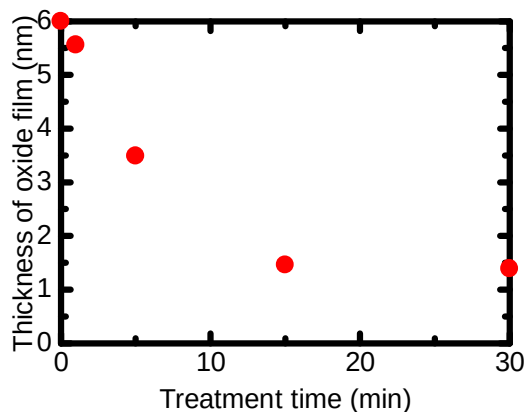


Fig.8. Hydrogen radical treatment time dependence of thickness of oxide film.

4. Conclusion

Improvement in flip-chip bonding by the reduction of oxides using hydrogen radicals was investigated.

The following results were obtained.

- (1) Hydrogen radicals could reduce the oxide layer on the Sn surface.
- (2) The hydrogen radical treatment was more effective in improving the flip-chip bonding than the conventional Ar plasma treatment.
- (3) When 100% hydrogen or ammonia was used as the source gas, hydrogen radical treatment for 1 min at the filament temperature of 1500 °C or more was effective in improving the flip-chip bonding without flux.
- (4) When the forming gas (N₂:H₂ = 96:4) was used as the source gas, hydrogen radical treatment for 15 min or more at the filament temperature of 1600 °C was effective in improving the flip-chip bonding without flux.

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