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A Study on the Fluxless Soldering of Si-Wafer/Glass Substrate Using Sn–3.5 mass%Ag and Sn–37 mass%Pb Solder

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UBM-coated Si-wafer was fluxlessly soldered with glass substrate in N_2 atmosphere using plasma cleaning method. The bulk Sn-37 mass%Pb and Sn–3.5 mass%Ag solders were rolled to the sheet of 100 μm thickness in order to achieve bonding to Si-wafer by fluxless 1st reflow process. The oxide layer on the solder surface was analyzed by AES (Auger Electron Spectroscopy). After 1st reflow the Si-wafer with a solder disk was plasma-cleaned, and soldered to glass by 2nd reflow soldering process without flux in N_2 atmosphere. The thickness of oxide layer decreased with increasing plasma power and cleaning time. The optimum plasma treatment condition in this study was 500 W for 12 min and at this condition, 100% bonding ratio for Sn–3.5 Ag and over 80% bonding ratio for Sn–37Pb solder were achieved. The intermetallic compound of continuous Cu_6Sn_5 was observed along the Si-wafer/solder interface but discrete Cu_6Sn_5 along the glass/solder interface and the different shapes of Cu_6Sn_5 were caused by different thickness of Cu as a pad. The fracture of the tensile test specimen occurred at not only solder/UBM and solder/TSM interface but also in Si-wafer and glass substrate.

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Keywords: *fluxless soldering, plasma cleaning, Silicon-wafer, glass substrate, oxide layer*

1. Introduction

The electronics assembly industry is forced to evaluate alternative methods to application of flux and Pb-containing solder during soldering process by the global concerns for environmental-friendly technology. The flux in soldering removes contaminants and dissolves surface oxides to improve wettability and solderability. The application of flux, however, could lead to the corrosion of the circuit and deterioration of the long-time reliability due to flux residues in the joint which may require cleaning after soldering.[1)] Especially in fine pitch flip chip package, the residual flux may exist in the region where inspection and removal of the residue are almost impossible.[2)]

The residual flux is generally cleaned by solvents such as chlorinated fluorocarbon(CFC), CFC-113. These volatile solvents are proved to have detrimental effect on the ozone layer.[3)] Since using flux causes environmental concerns manufacturer needs to find an effective replacement of flux. Therefore, fluxless soldering is becoming an active research area. There are several studies on the fluxless soldering such as plasma,[4)] laser[5)] and reducing gas[6)] treatment.

Plasma cleaning using energetic particles from a glow discharge is one of alternative methods to the application of flux. As a dry cleaning process, plasma treatment produces little or no waste byproducts, and is therefore far more attractive than solvent or acid based techniques where gallons of waste may be generated. The plasma treatment in soldering process is expected to eliminate the environmental concerns associated with solvent cleaning, flux and flux application system. However, plasma processing of materials has not been characterized to work properly in the soldering industry due to the difficulties in obtaining the optimum plasma conditions. The optimization problem is partly due to the large parameter space within plasma processing of materials and partly due to the complex nature of the plasma. The main process parameters are electrical power, gas flow rate/pressure, frequency and time.

In this work, the optimum plasma condition for fluxless soldering of Si-wafer/solder/glass substrate was assessed with the purpose of opto-electronic application. This paper reports the basic results of optimum plasma cleaning power and time in relation to the thickness of oxide layer of Sn–3.5Ag and Sn–37Pb solder and solderability of Si-wafer/solder/glass in fluxless N_2 reflow soldering.

2. Experimental

The P-type (100) Si-wafer and Schott 8330 glass substrate were used as the substrates for soldering. On Si-wafer 70 nm Cr layer was coated first, next 500 nm Cu and 50 nm Au for UBM (Under Bump Metallization) by E-beam evaporation. On glass substrate, 70 nm Cr layer was coated first, next 30 nm Cu and 50 nm Au for TSM (Top Surface Metallurgy). For solder, the bulk of Sn–3.5 mass%Ag and Sn–37 mass%Pb were rolled to the sheets of 100 μm thickness and the sheet was punched out into disk of 6 mm diameter.

Figure 1 shows schematically the overall experimental procedures. The solder disk was placed on the UBM-coated Si-wafer and reflowed (1st reflow) without flux in N_2 gas atmosphere. The wettability improvement by N_2 atmosphere has been reported on the same UBM as this work before.[7)] Purity of the N_2 gas was 99.999% and soldering peak temperatures were 260°C for Sn–Ag and 230°C for Sn–Pb. The heating rate is about 40°C/min and the time for the solder disk to be hold above eutectic temperature was 70 ~ 100 s. After the first reflow, the wetting angle was evaluated by cross-section SEM to evaluate the solderability. The solder on the Si-wafer was plasma cleaned to remove oxide layer, which formed on the solder surface during reflow process.

The RF Ar-plasma cleaning was used with the flow pressure of 0.14 MPa. The power supplied to sustain the plasma was changed from 200 to 600 W, and treating time from 1 to 12 min. The surface of the plasma-cleaned solders were ana-

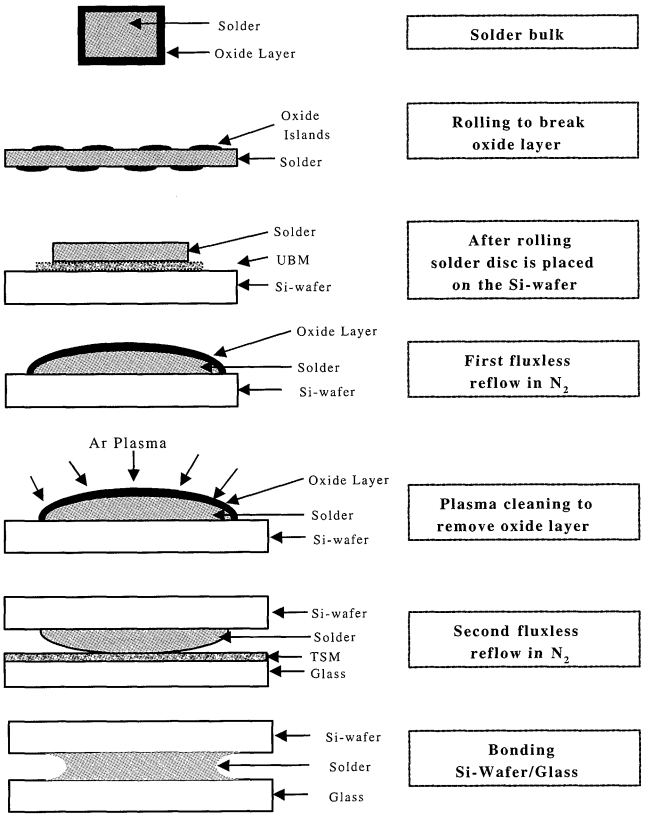


Fig. 1 Schematic illustration of experimental procedure.

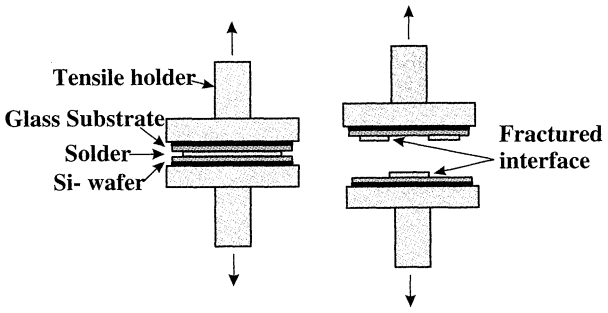


Fig. 2 Schematic diagram of the tensile test of solder joint.

lyzed through AES (Auger Electron Spectroscopy) depth profile to examine thickness of oxide layer on the solder surface. The etch rate of depth profile analysis was set to 5.5 nm/min for SiO_2. Plasma cleaned Si-wafer with solder was then reflowed (2nd reflow) with glass substrate in N_2 without flux under the same temperature profile as 1st reflow. After 2nd reflow, the cross section of the solder joint was examined and the bonding ratio between glass and solder was evaluated to estimated optimum plasma cleaning condition.

Tensile test for the Si-wafer/solder/glass solder joint was performed at a cross-head speed of 0.5 mm/s as seen in Fig. 2 to evaluate the mechanical strength and the fracture mode of the solder joint.

3. Results and Discussion

3.1 1st reflow and plasma cleaning

Figure 3 shows the wetted state of the solder disk to the UBM-coated Si-wafer after reflow in N_2 atmosphere without flux. The wetting angle of the rolled Sn–Pb and Sn–Ag solder disk was $9° \sim 10°$ at the edge of the triple point, which is the

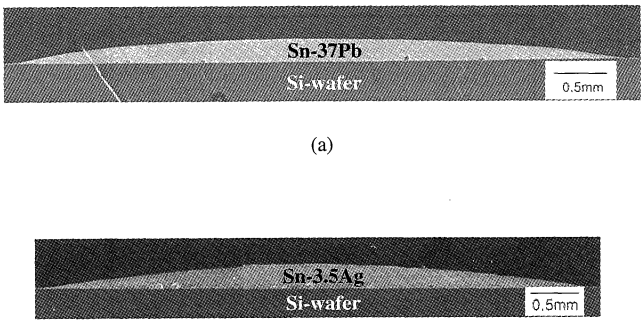


Fig. 3 Wetted state of rolled solder after fluxless 1st reflow (a) Sn–37 mass%Pb reflowed at 230°C (b) Sn–3.5 mass%Ag reflowed at 260°C.

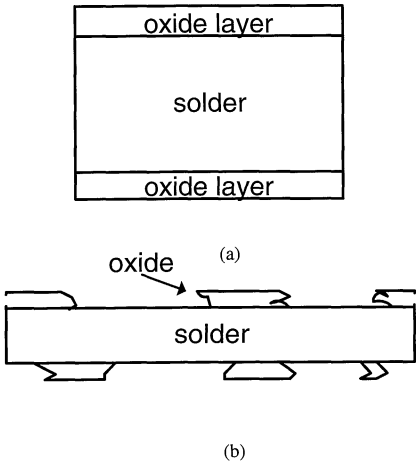


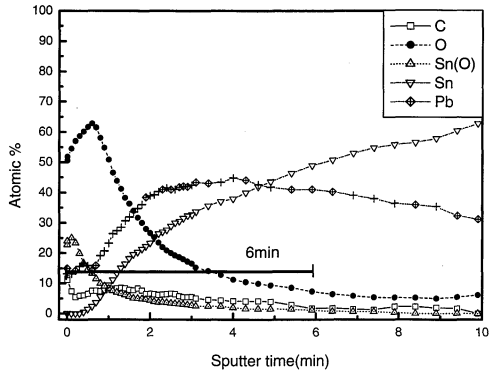
Fig. 4 Schematic diagram of solder before (a) and after (b) rolling.

same level as in case of using flux.[8,9] One explanation for the good wetting of the rolled solder disk may be that the oxide layer on the surface of solder is broken into smaller islands by rolling as schematically illustrated in Fig. 4, since oxide layer is more brittle but less ductile than solder. But the fuller study of fluxless soldering using rolled solder lies outside the scope of this paper and will be discussed in detail in another paper.

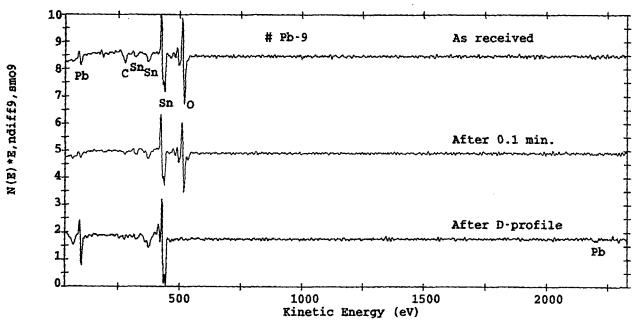
The oxide layer can be formed on the surface of solder during heating in 1st reflow soldering. In order to remove the newly formed oxide layer, plasma cleaning was performed on the 1st reflowed solder surface. The plasma-cleaned specimen shall be bonded to glass substrate by 2nd reflow soldering without flux.

Figure 5 shows AES depth profile of Sn–37Pb solder surface, which was plasma-cleaned with the power of 200 W for 1 min. From Fig. 5(a), it can be seen that it needs about 6 min sputtering for the O-content reaches to equilibrium state, and after the cleaning the oxide layer was completely removed in Fig. 5(b). In the next step, plasma-cleaning condition was changed to power of 400 W with treatment time of 10 min. The time to remove oxide layer from the Sn–37Pb solder surface was reduced to 4.5 min as shown in Fig. 6(a). As can be expected, the time to remove oxide layer decreased with increasing plasma power and cleaning time.

From the montage display of Auger depth profile of Sn[O] and Sn, it was possible to evaluate the time at which the Sn[O] peak transition to Sn peak begins and this time can be the measure for the time to remove oxide layer. The relationships

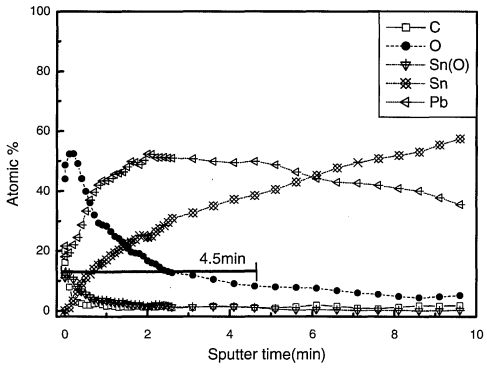


(a)

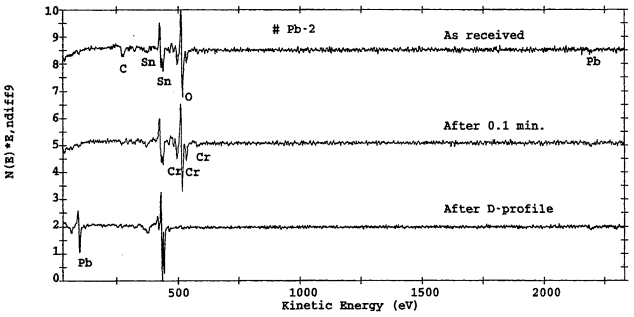


(b)

Fig. 5 AES depth profile for Sn–37 mass%Pb solder after plasma cleaning at power 200 W for 1 min. (a) Atomic percentage of the elements with sputtering time. (b) Differentiated Auger spectrum of the elements.



(a)



(b)

Fig. 6 AES depth profile for Sn–37 mass%Pb solder after plasma cleaning at power 400 W for 10 min. (a) Atomic percentage of the elements with sputtering time. (b) Differentiated Auger spectrum of the elements.

between plasma cleaning conditions and the Sn[O] → Sn peak transition time is given in Fig. 7. It can be summarized that the sputtering time for Sn[O] → Sn transition decreased with increase in power and cleaning time to the plasma condition of 500 W-10 min. Therefore plasma cleaning with higher power and longer time is more effective in removing oxide layer.

However, when the plasma cleaning condition became severe, with the power of 600 W for 10 min, the Sn–37Pb solder surface was damaged as shown in Fig. 8(a). As a result of the damage on the surface of solder, the transition time increased drastically in case of Sn–37Pb. The damaged surface was compared with the normal surface produced under the plasma condition of 400 W–5 min. In Fig. 8(a), the dark area on the damaged surface seems to be over etched by Ar plasma. The EDS analysis result showed the dark area is Sn-rich phase of the Sn–Pb eutectic microstructure. So it was confirmed that the Sn-rich phase is more preferentially etched than Pb-rich phase by Ar plasma which have been reported by Masahiko.[4] Considering the feasibility of the oxide removal and surface condition after plasma cleaning for the case of both Sn–3.5 Ag and Sn–37Pb solder, the power of 500 W was chosen for the appropriate plasma power condition in this study.

3.2 2nd reflow fluxless soldering of Si-wafer and glass substrate

After plasma cleaning of the 1st reflowed solder surface, the Si-wafer was fluxlessly bonded to glass substrate by the 2nd reflow soldering in N_2 atmosphere with the same thermal profile as 1st reflow. The plasma power was set to 500 W and the plasma treatment time varied from 6 to 12 min. The bonded Si-wafer/glass substrate was cross-sectioned and

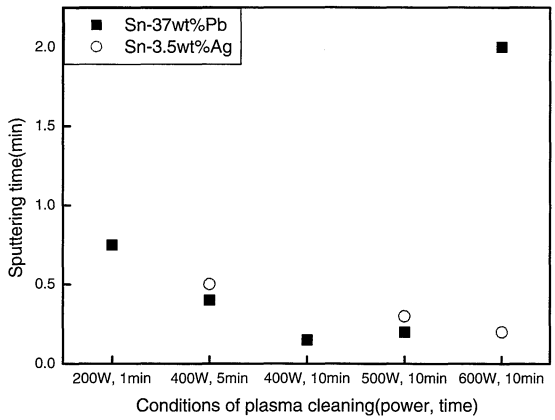
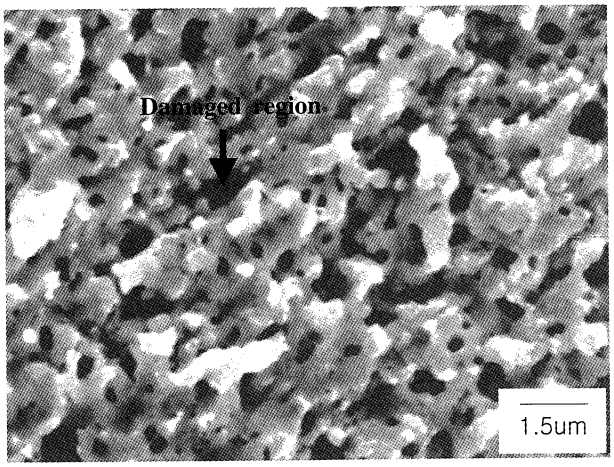


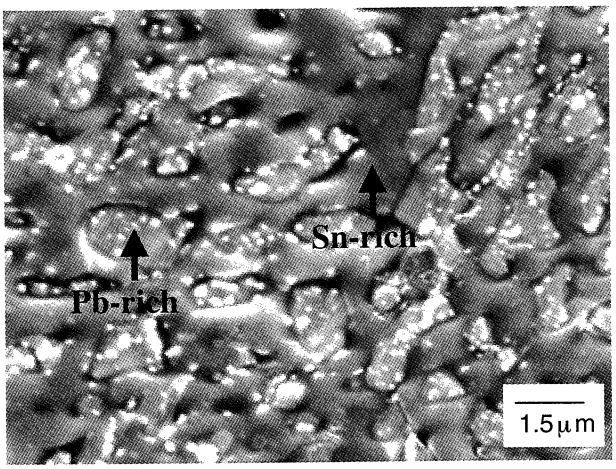
Fig. 7 Relationships between sputtering time for Sn[O] → Sn transition time by AES and conditions of plasma cleaning for the solder surface.

the interface between plasma treated solder and TSM-coated glass was observed to relate the plasma cleaning condition to the bonding ratio. Figure 9 shows the bonding ratio of fluxless solder joint of glass substrate according to the plasma cleaning condition for both Sn–3.5Ag and Sn–37Pb solder. The bonding ratio increased with plasma cleaning time and, for 12 minute-cleaning, the bonding ratio of 100% was obtained for Sn–Ag and over 80% for Sn–Pb solder.

Figures 10(a) and (b) shows the cross-section of the Sn–37Pb and Sn–3.5 Ag solder joint respectively formed between Si-wafer and the glass substrate after plasma treatment of 500 W–10 min. From the Fig. 10, we could observe that the solders have wetted the TSM of the glass substrate and a sound solder joint has been achieved by intermetallic compounds (IMC's) formation without flux. When the Sn–37Pb solder was plasma cleaned at 500 W–12 min and reflowed



(a)



(b)

Fig. 8 Damaged and normal surface for Sn–37 mass%Pb after plasma cleaning. (a) Damaged surface at 600 W for 10 min. (b) Normal surface at 400 W for 5 min.

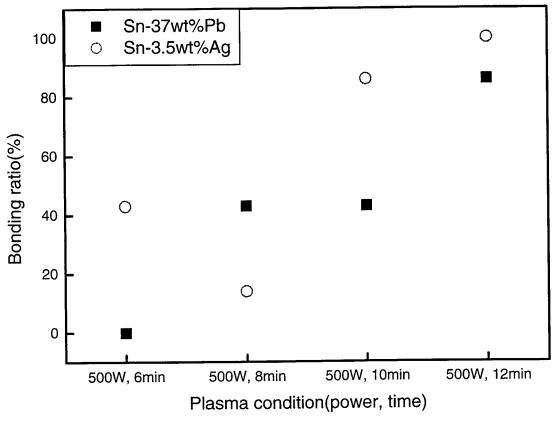
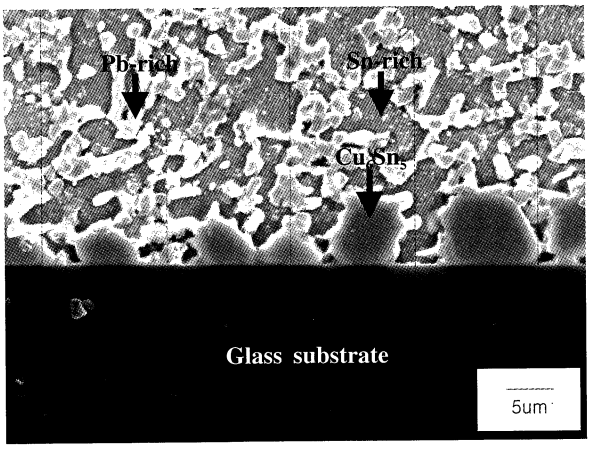


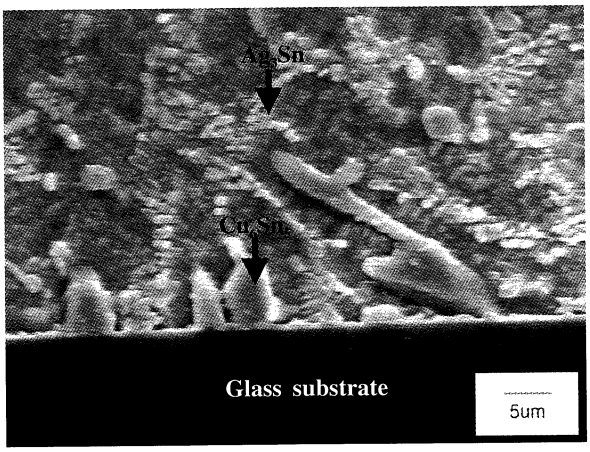
Fig. 9 Relation between bonding ratio (%) and plasma cleaning conditions.

to 230°C, round shaped Cu_6Sn_5 formed discretely along the interface as in Fig. 10(a). Figure 10(b) shows the discontinuously formed Cu_6Sn_5 IMC along the interface between Sn–Ag solder and TSM-coated glass substrate.

During soldering, Sn reacts with Cu and produces Cu_6Sn_5 IMC through consuming Cu. After 60 sec reflow, the consumed thickness of Cu is reported about 0.47 μm and 0.69 μm at 220°C and 240°C, respectively, and it is increased with time.[10] In this study, reflow temperature was 230°C and the



(a)



(b)

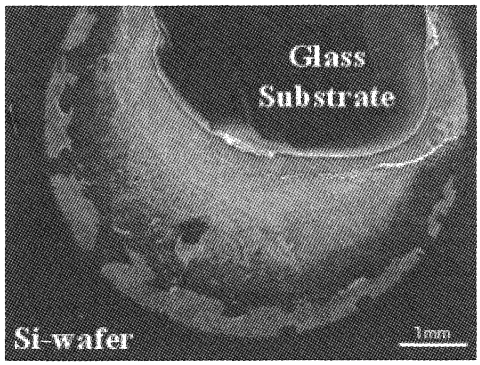
Fig. 10 Solder joint of Si-wafer and glass substrate after plasma cleaning at 500 W for 10 min. (a) Intermetallic compound formed at the interface between Sn–37 mass%Pb solder and glass. (b) Intermetallic compound formed at the interface between Sn–3.5 mass%Ag solder and glass.

reflow time is about 100 s for Sn–Pb and reflow temperature of 260°C for 70 s in case of Sn–3.5 Ag. The thickness of Cu on glass substrate is 0.3 μm. Therefore, the most Cu could be consumed. So, the Cu_6Sn_5 IMC might be spalled out discontinuously.

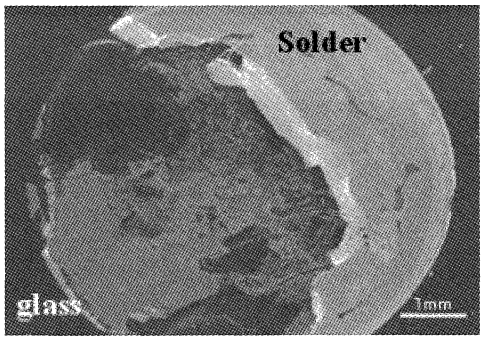
The increase of power for plasma cleaning makes it easier to remove the oxide layer on the solder surface but over critical point, the solder surface damage occurs. Also, the oxide layer becomes thinner for the longer plasma treatment time. However, the heat originated from the plasma could be flowed to the solder and substrate interface and cause the growth of the IMC as the effect of aging, which might be led to deterioration of the reliability. So, the Ar plasma treatment should be performed enough high power under critical value for short time.

3.3 Tensile test and fracture surface

Figure 11 represents the fracture surfaces of the Si-wafer/solder/glass substrate joint for plasma-cleaned Sn–37Pb and Sn–3.5Ag after tensile test at the cross-head speed of 0.5 mm/s. The tensile stress can occur in real service life to the bumps of the chip on board packages when the under-fill material between the die and substrate absorbs moisture and expands. The fracture of the joint showed the



(a)



(b)

Fig. 11 Fracture surface after tensile test for Si-wafer/solder/glass substrate joint. (a) Fracture surface after tensile test for Sn–37 mass%Pb soldere plasma-cleaned at 500 W for 12 min (tensile strength: 9.4 MPa). (b) Fracture surface after tensile test for Sn–3.5 mass%Ag solder plasma-cleanend at 500 W for 8 min (tensile strength: 10.3 MPa).

complex mode with the fracture between solder and UBM interface and the fracture of glass substrate in case of Sn–37Pb in Fig. 11(a). For Sn–3.5 Ag, the fracture occurred at solder/TSM interface and solder/UBM interface as can be seen in Fig. 11(b). The tensile strength of the Si-wafer/solder/glass joint was about 10 MPa. It could be said with fair certainty that the complex mode fracture of the joint is the evidence of the sound solder joint for Si-wafer/solder/glass substrate.

4. Conclusions

For the fluxless soldering of Si-wafer and glass substrate using rolled Sn–37mass% Pb and Sn–3.5mass% Ag solder disk, we used the plasma cleaning to remove the oxide layer on the solder surface and N_2 reflow soldering process. Plasma cleaning with higher power and longer cleaning time is more effective in removing oxide layer from the solder surface. However, the cleaning power condition over 600 W for 10 min can damage the Sn–37Pb solder surface. The optimum plasma treatment condition in this study is 500 W for 12 min and at this condition, 100% bonding ratio for Sn–3.5 Ag and over 80% bonding ratio for Sn–Pb solder were achieved. But the longer plasma treating time may cause the reliability problem due to the thermally activated intermetallic compound growth. Plasma treated Sn–37Pb and Sn–3.5Ag solder wetted the glass substrate well and a sound bonding could be obtained between Si-wafer and glass substrate without flux. The fracture of the tensile test specimen occurred at not only solder/UBM and solder/TSM interface but also in Si-wafer and glass substrate.

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