Understanding the Influence of Copper Substrate Oxidation on Silver Pressure Sintering Performance

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Abstract—Recently, due to the promising properties of silver, the low-temperature silver sintering joining technology has become increasingly attractive in power electronics. Reliable bonding quality of sintered silver depends not only on the microstructure, but also on the interfacial properties to the joining materials. Sintering on precious metal surfaces such as silver or gold works very well due to the good interdiffusion behavior of these elements. Non-precious metal surfaces such as copper are preferred to reduce manufacturing costs as no additional surface metallization layer is required. Sintering on copper surfaces is usually performed in a nitrogen atmosphere, as they can potentially oxidize during sintering in an oxygen-containing atmosphere. The resulting copper oxide is proposed to act as a diffusion barrier, resulting in weak bonding of the silver compound to the copper surface. In this work, we observed that not only the substrate oxidation during sintering, but also the initial Cu oxide layer affects the bonding performance. Therefore, different copper oxidation methods were performed to produce different types of copper oxides and thicknesses on active metal brazed (AMB) substrates. X-ray photoelectron spectroscopy (XPS) measurements of the samples indicate the presence of two types of copper oxides, which further affect the bond strength of sintered Ag differently. Pressure sintering with micron Ag paste on a nearly oxide-free copper surface produces lower bond strength than sintering on oxidized substrates. The highest bond strength can be achieved on CuO, but the presence of Cu₂O also contributes to the bonding of silver to the copper surface. If the oxide layer becomes too thick, bonding is no longer guaranteed. Higher sintering temperature and pressure results in a denser sintered layer and stronger bonding on copper substrates.

Keywords—pressure sintering, copper oxide, interdiffusion

1. INTRODUCTION

Recent trends in power electronics towards higher power densities and higher operating temperatures by using wide bandgap semiconductors require the development of alternative interconnect technologies between semiconductor devices and metal-ceramic substrates (MCS). Wide bandgap semiconductors enable efficient operation at high temperatures ranging from 200 °C up to 350 °C [1, 2]. In such harsh environments, lead-free solder materials reach their limits. Due to their toxic properties, environmental regulators have banned the use of lead-containing materials in electronic products since 2006 [3]. As operating temperatures rise above 200 °C, the strength and reliability of lead-free solder materials decrease [4], and soldering is gradually being replaced by silver sintering in packaging and connection technology [5].

The low temperature joining technology of silver sintering has attracted remarkable attention in recent years due to the promising properties of silver. Silver sintering materials are ideally suited as an alternative joining material to soft solders due to their excellent properties such as high melting temperature at relatively moderate process temperatures and high thermal and electrical conductivity [3, 5].

Substrates with excellent heat dissipation properties and good mechanical stability are also required for high-power electronic devices. In recent years, silicon nitride has been considered as one of the best ceramic substrate materials due to its high thermal conductivity and its mechanical properties [6]. Silver sintering in combination with active metal brazed (AMB) Si₃N₄ substrates can fully utilize the potential of silver sintering and achieve the highest reliability.

Silver sintering is well established on noble surfaces such as silver and gold, since the Ag-Ag self-diffusion and the Ag-Au interdiffusion are known to be much faster than the Ag-Cu interdiffusion [7]. Several studies have shown that very strong silver-silver bonds can be formed using pressure-assisted and pressureless sintering processes [8–10]. Ag precious metal plating on substrates leads to high manufacturing costs, so bare copper substrates are preferred. In [8], Wang et al. discussed different commonly used surface metallization layers in terms
of their bonding strength and demonstrated the technical challenge of sintering on copper surface with respect to substrate oxidation during air sintering. In contrast, some studies have shown that the copper oxide layer generated during sintering in air helps to bond silver to the surface and acts as an adhesive [11, 12], but there is limited research on the influence of the initial copper substrate oxidation on silver pressure sintering performance. To focus on this issue, we created different copper oxides and oxide thicknesses on AMB substrates and performed silver pressure sintering in a nitrogen atmosphere on these oxidized surfaces. In addition, XPS measurements were used for surface characterization. To investigate the bond strength, die-shear tests were performed on the sintered samples with copper oxide variations in relation to an almost oxide-free surface. Spectroscopic and microscopic methods were used to study the microstructure, the structure of the Ag-Cu interface and the fracture surface after the die shear test.

II. EXPERIMENTAL

A. Materials

Bare copper active-metal-brazed Si₃N₄ substrates with a size of 27 x 38 mm and a copper sheet thickness of 0.3 mm were used as the base material. A commercially available silver sinter paste (Heraeus ASP 338-28) containing Ag particle sizes of 1-20 μm, solvents and organics was used as the interconnect material. Non-functional silicon dies of 4 x 4 mm size with 700 nm Ag backside metallization and 250 μm thickness were used for die attach.

B. Substrate oxidation processes

Each substrate has individual surface characteristics due to variations in manufacturing processes and packaging materials. For reproducibility and comparability, the copper AMB substrates were cleaned with formic acid immediately prior to use. The cleaning process was performed with a PINK Vadu 200 soldering system. Subsequently, oxygen plasma generated by the plasma system AP-600 of Nordson-March was used to create different copper oxide thicknesses on the AMB surfaces by varying the oxidation time from 3 min, 5 min, 7 min, 10 min to 15 min, see Fig. 1(a). Base pressure, process pressure and gas flow were kept constant. Thermal oxidation in a convection oven for 3 min, 5 min, 10 min and 15 min at 160 °C in air was used as an additional oxidation method. As shown in Fig. 1(a-b), the surface color changes due to the plasma and thermal oxidation treatments.

a)  

b)  

Fig. 1. AMB substrates after a) plasma oxidation for 0, 3, 5, 7, 10, 15 min and b) thermal oxidation for 0, 3, 5, 10, 15 min.

C. Sample preparation

The sample preparation steps are shown in Fig. 2. Silver sinter paste was printed on the oxidized substrates using a 150 μm stencil with 8 opening pads for die attach. After paste application, the printed paste was dried in a convection oven to evaporate the solvents. The drying parameters were set at 140 °C for 20 min in nitrogen atmosphere. After drying process, Si dies were attached onto the dried sinter pads with a force of 2000 g and an attachment time of 2000 ms. To ensure that the semiconductor device adheres well to the dried paste before it is transferred to the pressure sintering process step, the placement is performed at elevated temperature, in this case, 75 °C, in order to prevent oxidation of the copper substrate. Pressure sintering process was performed after die placement. Oxygen plasma treated and thermally oxidized substrates were sintered in a sinter press with different sintering conditions to compare sintering performance with respect to different oxide thicknesses and types. Moderate sintering parameters of 230 °C temperature, 10 MPa pressure and 3 min sintering time were used as well as 250 °C, 20 MPa for 3 min. Two substrates were prepared for each parameter setting and oxide surface, see Fig. 3.

D. Characterization Methods

Before and after substrate oxidation, X-ray photoelectron spectroscopy was performed using PHI VersaProbe 4 equipment. XPS analysis provides information about the surface chemistry of the material and allows depth profiling through the integrated ion gun. Relevant regions considered here were Cu 2p, O 1s, C 1s, and Cu LMM, where detailed spectra and depth profiles were measured with an argon sputtering time of 15 x 2 min and 10 x 4 min (1 kV on 2 x 2 mm). C-C/H component of the C 1s region serves for referencing and was set to 284.8 eV since the neutralizer in XPS equipment leads to an instrument dependent shift in the binding energies. Using fitting models from the literature, the oxide thickness of oxidized samples could be estimated from XPS data. Sintered samples were subjected to a die shear test (Nordson Dage 4000 plus) to evaluate the bond strength of the silver sinter joint on the AMB substrate with respect to the initial copper oxide surface. Fracture mode inspection with light microscopy shows if and where bonding has occurred. A distinction is made between
cohesive, adhesive, and mixed fractures. Cohesive fracture is desirable and indicates a strong bond at both interfaces, as the sintered layer is the weak bond. Adhesive fracture is less desirable as it indicates poor bonding to the interfaces. In addition, mixed fracture can occur where paste residues are found on both the backside of the chip and the top side of the substrate. In addition to optical microscopy, scanning electron microscopy (SEM) was applied to the fracture surface of both the AMB substrate and the silicon die backside after the die shear test to investigate the adhesion behavior. EDX mapping of both fracture surfaces was used to measure residues of the elements C, O, Cu, and Ag, the amounts of which can indicate the bond quality. Cross-sections of sintered samples were examined by SEM to study the silver-copper oxide/copper interface in detail.

III. RESULTS AND DISCUSSION

A. Oxide layer analysis of AMB surfaces by XPS analysis

The chemical compositions and bonding states on the surfaces of the substrates were analyzed by XPS after AMB cleaning and subsequent oxidation. A copper AMB substrate with a natural oxide layer (stored at room temperature for a few months) was also measured to compare the surface with the oxidized ones. Fig. 4 shows the survey spectrum of a copper AMB substrate with a naturally oxidized surface, which shows several distinct peaks that can be attributed to copper, silver, oxygen, and carbon. The silver is due to the AMB manufacturing process and the carbon is due to surface contamination. To evaluate the copper oxidation state, detailed spectra of the regions Cu 2p, O 1s, and Cu LMM were measured. Furthermore, the C 1s region was studied as reference for the binding energies. The spectra are not shown because no variation related to the oxidation method could be found.

Fig. 4. Survey spectrum of a naturally oxidized copper AMB substrate.

Fig. 5 and 6 compare detailed spectra of Cu 2p and O 1s for four surface states: cleaned (0 min), naturally oxidized, plasma oxidized for 10 min, and thermally oxidized at 160 °C for 10 min. Looking at the Cu 2p region in Fig. 5, we can clearly identify two different dominant copper oxide species with respect to both oxidation processes. The main Cu 2p3/2 peak position in Fig. 5(c) is at 933.8 eV and represents the dominant Cu(II) species in CuO. This spectrum also shows characteristic strong shake-up peaks in contrast to the spectra in Fig. 5(a-b, d), confirming the presence of CuO after plasma oxidation. Overlapping peak positions within the main Cu 2p3/2 peak for metallic Cu(0) and the majority of Cu(II) species (both about 932.5 eV) make it difficult to clearly distinguish these components which dominate the cleaned, naturally oxidized and thermally oxidized surfaces. The results of the O 1s spectra shown in Fig. 6 agree very well with the results from the Cu 2p region. In all samples, we find five characteristic peaks which can be assigned to O-C/O-H bonds (535.5 eV), O in the lattice of CuO (530.2 eV), O in the lattice of CuO (529.7 eV) and in both cases a smaller peak related to defect sites in the oxides according to [13]. The O 1s region of the clean surface (Fig. 6(a)) and the naturally oxidized surface (Fig. 6(b)) show similar components, only the proportion of O in CuO is larger in the latter due to oxidation during storage. Fig. 6(c-d) show large differences in the spectra due to the oxidation process. While thermal oxidation leads to an increasing amount of CuO bonds, plasma oxidation produces predominantly CuO.
Clear identification of the dominant copper species in the four sample surfaces is accomplished by evaluation of the corresponding Cu LMM Auger spectrum, shown in Fig. 7. Copper and its binary material systems show characteristic Auger electron spectra. For Cu(0), Cu$_2$O and CuO, the maximum of the Auger spectrum is at a kinetic energy of 918.6 eV, 916.9 eV, and 917.8 eV, respectively. In the corresponding fit model, Cu(I) and Cu(II) species were not distinguished. Their superposition helped to identify the maximum peak value to determine copper oxidation state or copper species, respectively. Looking at Fig. 7(a), we can distinguish between Cu(0) and Cu(I), both of which are present in the purified state. By storage at room temperature and thermal oxidation, Cu(I) is mainly formed on the copper surface, which is represented by the peak maximum at about 917 eV in (b) and (d). The Cu(I) species becomes thicker due to thermal oxidation as the Cu(0) intensity at the sample surface becomes smaller, see Fig. 7(d). Plasma oxidation causes a peak shift to a higher kinetic energy in the Cu LMM spectrum to about 918 eV, indicating the formation of Cu(II). Fig. 8 shows a Wagner plot of the position of the maximum peak value of the Cu LMM region (kinetic energy) as a function of the position of the maximum of the Cu 2p3/2 signal (binding energy) to summarize the XPS data and compare it with literature data from [13]. We can assign the measured peak intensities of the considered surfaces to the different copper species. The natural oxide layer consists mainly of Cu$_2$O, as well as the oxide generated by thermal treatment. In contrast, plasma treatment leads to the formation of CuO on the copper surface.

Depth profiling was used to observe the layer structure as a function of depth. Fig. 9 shows the depth profiles of Cu and O for six samples that were thermally treated for different times in (a) and (b) and plasma treated for different times in (c) and (d). The naturally oxidized sample is plotted as a reference material (a-d). The color scale indicates the corresponding treatment time. Cu fractions are plotted in (a) and (c), the O fractions in (b) and (d). In all samples it can be observed that the oxide layer is only present at the surface, since with increasing sputtering time the relative Cu concentration approaches the maximum of <99.0% and the relative O concentration approaches <1.0%. The sputtering time correlates linearly with the depth, so it can be assumed that the oxide thickness increases with plasma or thermal oxidation time. Comparing not only the samples within a test series, but also the test series themselves, it can be seen that the oxide thickness between the two series differ. For the plasma oxidation process of 15 min, 600 s of etching time is required, whereas for the thermal oxidation process of 15 min, only 400 s etching is sufficient to reach the pure copper state.
In addition, the oxide layer thicknesses were calculated from the relative compositions of Cu(0), Cu$_2$O and CuO by using the equation explained in [13], see Fig. 10. The relative compositions were estimated by fitting the Cu LMM region with the fitting parameters described in [13]. The cleaned, nearly oxide-free surface shows a calculated oxide layer thickness of 1.75 nm which can be explained by the immediate reaction of copper on contact with oxygen. The layer thickness of the naturally oxidized sample is calculated to be 2.54 nm, which is in the same range as the thermally oxidized samples, since both are dominated by Cu$_2$O species. The thermally generated Cu$_2$O dominated surfaces start with a oxide thickness of 2.45 nm after 3 min heating to 3.25 nm after 5 min heating and do not increase further, although the copper color changes as already shown in Fig. 1(b). CuO dominated surfaces generated by plasma oxidation have a minimum oxide thickness of 4.20 nm after 3 min treatment and end up with 8.13 nm after 15 min treatment. The latter value is not shown in the graph and was estimated by calculation from the depth profiles. It is important to note that all values are only estimates from the measured data and contain measurement inaccuracies.

![Fig. 10. Estimated oxide layer thicknesses of naturally oxidized, cleaned, plasma oxidized and thermally oxidized surfaces of Cu substrates. Calculation equation and fitting parameters were used from [13].](image)

**B. Ag joint bonding performance on oxidized surfaces**

Fig. 11 shows the shear strength of the samples sintered with different parameter settings with respect to the increasing time of the plasma oxidation process. The presence of Cu oxide improves the bond strength to a maximum value of 78.7 N/mm$^2$ (250 °C, 20 MPa, 3 min) and 54.3 N/mm$^2$ (230 °C, 10 MPa, 3 min) after 5 min oxidation time, respectively. With even longer oxidation time, the shear strength decreases drastically with low sintering temperature and pressure. With highest sintering pressure and temperature, the shear strength shows only a slight decrease up to 10 min oxidation time and it decreases significantly to a value of 33.6 N/mm$^2$ after 15 min. The results indicate a strong influence of the copper substrate surface layer on the bond performance. Furthermore, sintering parameters affect bonding performance on oxidized substrates. An additional parameter setting of 230 °C, 20 MPa, 3 min shows that particularly pressure is required to ensure strong adhesion at higher oxide thicknesses.

![Fig. 11. Comparison of die shear strength before and after plasma oxidation. The triangular, diamond and square curves represent the sintering parameters of 230 °C, 10 MPa, 3 min, 230 °C, 20 MPa, 3 min and 250 °C, 20 MPa, 3 min, respectively.](image)

![Fig. 12. Comparison of the fracture patterns after die shear test before and after plasma oxidation. Samples were sintered in a) at 250 °C, 20 MPa, 3 min, in b) at 230 °C, 20 MPa, 3 min and in c) at 230 °C, 10 MPa, 3 min.](image)
The shear strength of the samples sintered at 250 °C, 20 MPa, 3 min (squares) and 230 °C, 10 MPa, 3 min (triangles) with respect to increasing thermal oxidation time is shown in Fig. 13. We observe a slightly increasing bond strength with increasing oxidation time for low parameter settings. At higher temperature and pressure, the shear values are relatively equal within the range of variation. The latter result in stronger bonds, but not as high as for the plasma oxidation process (Fig. 11). The small changes in shear strength from 5 min to 15 min thermal oxidation can be explained by the nearly identical estimated oxide thicknesses. The failure mode is like the results already shown in Fig. 12, with a slight increase in cohesive failure near to the substrate surface.

Fig. 13. Comparison of die shear strength before and after thermal oxidation. The square and triangular curves represent the sintering parameters of 250 °C, 20 MPa, 3 min and 230 °C, 10 MPa, 3 min, respectively.

Since we know the corresponding estimated oxide layer thicknesses as well as the dominant oxide species of all samples from XPS, they can be correlated with the shear strength results. Fig. 14 shows the bond strength of the sintered samples as a function of the estimated oxide thickness, including the dominant oxide species. It can be concluded that at the maximum Cu$_2$O thickness of about 3.0 nm generated by the thermal oxidation process, the shear strength can be increased for both parameter settings, but more significant for the low sintering parameter settings (36.4% increase). At higher oxide thicknesses generated by plasma oxidation of about 4.0 nm to 4.5 nm, dominated by CuO, the maximum bond strength can be achieved, characterized by an increase of 36.6% and 54.3% for high and low parameter settings, respectively. Therefore, the bond performance is very sensitive to minimal changes in the copper surface condition, especially for mild sintering conditions. This is also demonstrated by the small increase in shear strength at low oxide thicknesses for high sintering temperature and pressure (7.6%), because here the process parameters are high enough to produce a strong bond regardless of the surface condition. In this case, further surface modification helps to significantly improve the bond performance. As the oxide thickness increases, the bond quality decreases again.

Fig. 14. Comparison of die shear strength with respect to the estimated copper oxide thicknesses and dominant oxide species. The square and triangular curves represent the sintering parameters of 250 °C, 20 MPa, 3 min and 230 °C, 10 MPa, 3 min, respectively. Cu$_2$O species generated by thermal oxidation is marked in grey, CuO species generated by plasma oxidation is marked in black.

C. Ag layer microstructure and interfaces

The microstructure of the silver sintering material was investigated via SEM using ion-etched cross-sections. Fig. 15 compares the Ag layer microstructure of both sintering processes in the initial stage (cleaned). It is clearly visible that higher sintering parameters lead to densified silver layer and is one of the main reasons for higher bond strength. Mild pressure and temperature are not sufficient for strong Ag-Ag necking as we still can identify the silver flake powder structure and lower densification, see Fig. 15(a). The microstructure is independent of the copper surfaces oxidation state and remains the same.

Fig. 15. Cross-sectional SEM image at 30kx magnification showing the microstructure of the silver layer sintered in a) at 230 °C, 10 MPa, 3 min and in b) at 250 °C, 20 MPa, 3 min, respectively.

For high sintering parameters, a large area of silver bonding to the copper surface was observed. Therefore, higher process parameters result not only in denser Ag layer but also in stronger bonding to the surface. Looking at the Ag-Cu interface of a sintered sample on a 10 min plasma oxidized surface, the direct connection of silver and copper grains is detectable, confirming that silver can attach to the oxidized copper surface, see Fig. 16. In contrast, the presence of a copper oxide layer after sintering could not be clearly identified by SEM. The material contrast of Ag-Cu is almost the same as that of Ag-Ag grains, making it difficult to see the oxide clearly. Additional characterization methods such as transmission electron microscopy (TEM) are required for identification.
D. Fracture surface investigation by SEM and EDX analysis

SEM images at different magnifications of samples sintered on plasma and thermally oxidized AMB substrates as well as EDX measurements of both fracture surfaces, the die backside and the substrate surface, were investigated. In the latter, the elements C, O, Cu and Ag were found. A representative EDX measurement and evaluation of the substrate surface after 10 min plasma oxidation is shown in Fig. 17. The carbon is due to contamination from sample handling and organic residues from the paste. In contrast to the substrate surfaces, there is almost no detectable Cu or O concentration on the backside of the die. The slight cohesive failures in the sinter joint of all samples with weak bonding to the substrate surface is indicated by the low amount of Ag residues detected, with a maximum of 34.3 wt% for high and 29.3 wt% for low parameter settings, respectively. To clarify the influence of process parameters, SEM images of fracture surfaces on 10 min plasma oxidized substrates are shown in Fig. 18 and Fig. 19 with respect to the sintering process. With low sintering pressure and temperature, we see only sporadic Ag particles on the copper surface (Fig. 18(a-b)) and a loose particle layer on the chip backside (Fig. 18(c-d)). In contrast, more Ag necking on the copper surface is shown in Fig. 19(a-b), where higher pressure and temperature were used for the sintering process. Looking at the backside of the chip (Fig. 19(c-d)), a slight deformation of the particles in the shear direction can be seen, indicating strong Ag bonding.
In the present work, the influence of copper substrate oxidation on silver pressure sintering performance in nitrogen atmosphere was investigated. The surface conditions of copper AMB substrates can be modified by plasma oxidation process or thermal treatment. Substrates treated thermally generated a thinner oxide layer dominated by Cu2O species than those treated by plasma, whose surfaces are mainly composed of CuO, as detected by XPS. Considering all the results, the following conclusions can be drawn. Sintering on copper substrate in a nitrogen atmosphere results in a slight cohesive failure at the substrate interface, as evidenced by the low amounts of Ag residues after the die-shear test at the substrate surface measured by EDX. Increased bond strength results in stronger cohesive failure and mixed fracture patterns, which can be achieved by modifying the surface of copper AMB substrates with a thin copper oxide layer up to 4.50 nm by plasma oxidation. Depending on the sintering process parameters, the shear strength can be improved up to 36.6% and 54.3%, respectively. The application of higher temperature and pressure leads to improved bond performance due to higher densification, as demonstrated by cross-sectional SEM images. Decreasing bond strength occurs when the copper oxide is too thick (>5.00 nm). It is clearly demonstrated that the bonding performance of a silver sinter paste on Cu-AMB substrates can be improved by forming a thin nanoscale copper oxide layer on the initial substrate surface. Due to the formation of two different dominant copper oxide species that do not have comparable thicknesses, it is still not fully understood which oxide species has a significant influence on the sintering performance. Therefore, the bonding mechanism needs to be further investigated with additional characterization methods such as TEM to identify the species generated at the interface, as it is rather difficult to identify the copper oxide layer by SEM.

IV. SUMMARY

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V. REFERENCES