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Interfacial Interactions Between W_xN Substrates and a Gold-Tin Alloy

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Au-Sn is an excellent material with superior attributes and is the solder of choice, with no obvious alternatives, in many microelectronic applications. Recently, this alloy has been chosen as a potential candidate for bonding in wafer level hermetic packaging at high temperature using WN as diffusion barrier. In this application, good wetting of WN by the liquid Au-Sn alloy is a key factor for the bonding process. To this end, wetting of W_xN (covered or not by a gold layer) by Au-Sn20 alloy was studied at 380 °C under high vacuum. Excellent wetting was observed when W_xN was protected from oxidation by a thin Au layer. The spreading process was found to be followed by a complete dissolution of a protection layer and slight receding of the triple line. Some preliminary bonding tests using Au-Sn alloy were also performed.

Keywords Au-Sn solder, MEMS packaging, tungsten nitride, wetting

1. Introduction

Wafer level packaging needs a hermetic bonding solution to address microsystems requiring a controlled atmosphere surrounding the device. Various wafer level packaging methods are summarized in Ref 1. One of these methods is the bonding method with molten materials and especially by using solder or other conductive molten material. Soldering and eutectic bonding can be applied to the wafer level packaging by thermally melting metals.

Eutectic Au-Sn solder alloy is of proven utility for integrated circuit chips or die bonding because of its high bond strength, good adhesion, low stress, corrosion resistance, and good thermal conductivity; it is increasingly used in high temperature and/or high reliability applications due to excellent mechanical and thermal properties and its ability to be reflowed without flux (Ref 2-5).

These applications include hybrid microelectronics (particularly flip chips), MEMS, optical switches, RF devices, and hermetic packaging for various applications. On top of these applications, AuSn provides the additional benefit of not requiring flux during reflow, significantly reducing the potential for contamination and pad corrosion. However, the materials and processing considerations are substantially different than for conventional solders. Recently, gold-tin eutectic bonding was investigated for 200 mm wafer level hermetic packaging (Ref 6) using WN or Ni as diffusion barrier layer. Belov et al. (Ref 3) have tested different adhesion and barrier layers to find a good trade-off between bond strength, gap control, and hermeticity. A Nb/Au film was shown to be a good seed layer candidate. As Nb is not widely used in microelectronics, WN or Ni are more suitable as adhesion and barrier layers. Indeed, tungsten nitride is considered to be a good barrier against the diffusion of copper in microelectronic circuits (Ref 7, 8). A good wetting of the diffusion barrier by the soldering alloy is necessary to have a good joining. To our knowledge, no study exists on the wetting of the tungsten nitride by liquid Au-Sn alloys.

The aim of this work is to study the wetting of tungsten nitride W_xN (x = 1, 2 and x = 2) by the gold-tin eutectic alloy in two configurations: (i) the tungsten nitride is covered by a protective thin gold layer and (ii) not covered by a protective gold layer.

2. Experimental Procedure

Wetting was studied by the dispensed drop method, in a metallic furnace under a vacuum of $(1 \text{ to } 5) \times 10^{-5}$ Pa at 380 °C. In the "dispensed drop" technique, the experiment involved heating an Au-Sn in an alumina crucible placed above the substrate. At the experimental temperature, the liquid is extruded from the crucible through a capillary with internal diameter of 0.6 mm and put in contact with the substrate. This technique allows the process of melting and spreading to be separated so that fully isothermal experiments can be performed.

The wetting process is filmed by a video camera (25 frames per second) connected to a computer, enabling automatic image analysis. The characteristic dimensions of the drop (drop base

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radius *R* and contact angle θ) are extracted with an accuracy of ±2° for θ and ±2% for *R*.

The Au-Sn (20 wt.%) alloy—noted AuSn20 (purity higher than 99.99%) was supplied by Goodfellow as a wire of 500 µm in diameter. The substrates used in this study are multilayered and consist of the silicon wafer with the 500-nm-thick Si oxide layer covered by the under-bump-metallurgy layer which comprises an adhesion Ti layer (200 nm) and a W_xN ($W_{1.2}N$ or W_2N) diffusion barrier layer (50 nm) deposited by sputtering under vacuum. Several substrates were also covered by a protective Au layer also deposited by sputtering (see Fig. 1). Hereafter the substrates without Au coating will be referred to as $W_{1.2}N$ and W_2N and those with Au coating as $W_{1.2}N$/Au and W_2N/Au.

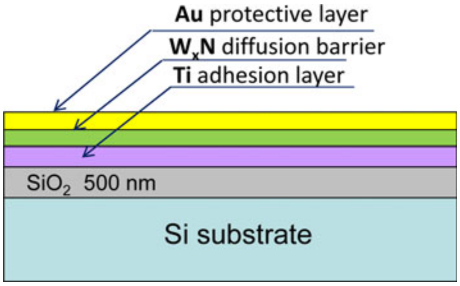

Fig. 1 Schematic representation of the Si/Ti/W_xN/Au system

W_xN is known to be very sensitive to oxidation. Characterization of the W_xN surface before the wetting experiments was performed by X-ray photoelectron spectroscopy (XPS).

After the wetting experiments, the selected specimens were cut perpendicularly to the interface for SEM observation.

3. Results and Discussion

3.1 Wettability of W_xN and W_xN/Au by AuSn Eutectic

The first set of the wetting experiments was performed with the substrates not covered by the Au layer and having as an upper layer $W_{1.2}N$ or W_2N coating (see Fig. 1). Figure 2 provides the lateral images of the AuSn20 drops formed, respectively, on $W_{1.2}N$ and W_2N, 40 ms after deposition. In both cases the contact angles are very close and equal to 130° ± 2°. Note that these angles did not change with time during 15 min of the isothermal hold. Such high values of contact angle presumably can be attributed to the oxidized W_xN surfaces (Ref 9). In order to validate this assumption both surfaces were analyzed by XPS and the spectra obtained are given in Fig. 3. The observed peaks have been perfectly deconvoluted by using the signals proper to the W-N (blue) and W-O (yellow) bonding. The presented spectra clearly show the presence of tungsten oxide on the W_xN surface when it is not protected by the Au layer. The oxide layer covering the substrates appears to be stable during the isothermal hold thus ensuring the non-reactive wetting. Such behavior obviously can

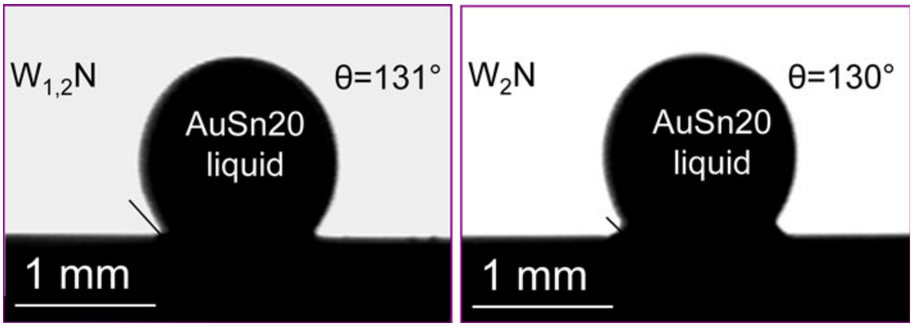

Fig. 2 Lateral images of the AuSn20 drops formed, respectively, on $W_{1.2}N$ and W_2N, 40 ms after deposition. T = 380 °C

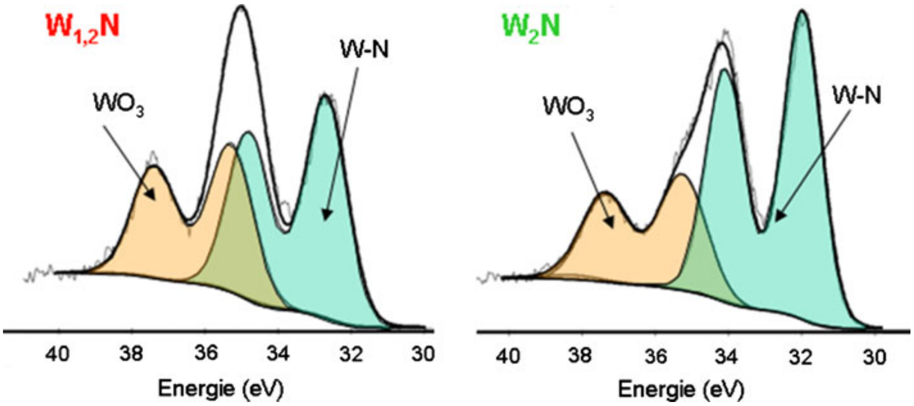

Fig. 3 X-ray photoelectron spectroscopy and the spectra obtained for $W_{1,2}N$ and W_2N surfaces. The observed peaks are deconvoluted by using the signals proper to the W-N (blue) and W-O (yellow) bonding

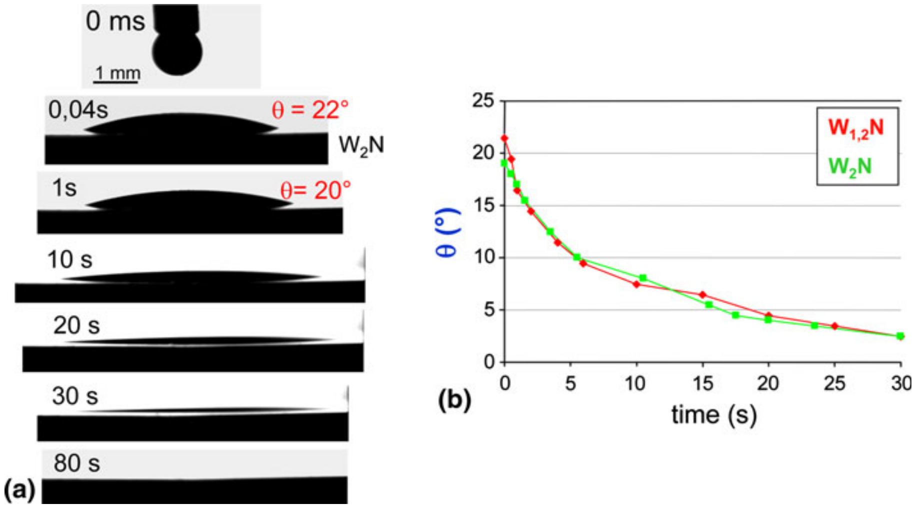

Fig. 4 Selected images of the drop profiles taken during its spreading over the W_2N/Au substrate (a) and evolution of the contact angle with time for both substrates (b)

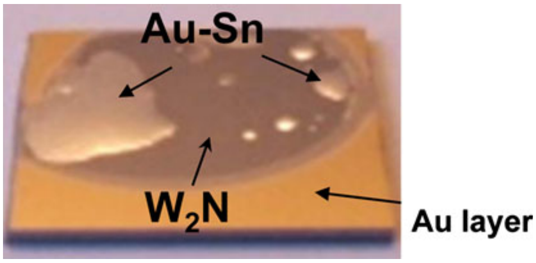

Fig. 5 Optical image, at room temperature, of the AuSn20/Au/W_2N sample after a wetting experiment at 380 °C

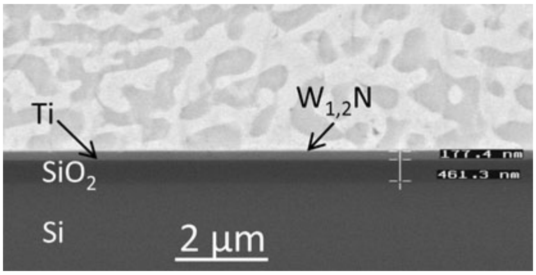

Fig. 6 SEM micrograph of a cross-section of the AuSn20/Au/$W_{1,2}N$ sample after a wetting experiment at 380 °C

not be favorable for successful joining. Effective W_xN surface deoxidation could be performed by thermal annealing during several hours in vacuum at high temperature (>1000 °C). However, such a treatment is not convenient for the substrate under study for the reason that W_xN is no longer active as a diffusion barrier after any heat treatment at temperatures higher than 600 °C. The only way to protect the W_xN layer from native oxidation is to cover it by a gold protective layer.

The second set of the wetting experiments was done with the substrates covered by a 100-nm film of gold ($W_{1.2}N$/Au and W_2N/Au). Figure 4 provides the selected images of the drop profiles taken during its spreading over the W_2N/Au substrate (a) as well as the evolution of the contact angle with time both for $W_{1.2}N$/Au and W_2N/Au ones (b). In both cases the spreading kinetics is very similar, with the first contact angle measured after 40 ms of contact being in the range of 18°-23°. Afterwards the contact angle decreases relatively slowly, attaining 17° ± 2° after 1 s and 4° ± 2° after 20 s of spreading. After that time, the triple lines of the drops were no longer distinguishable in the camera view due to a very low contact angle.

The sample inspection after the wetting experiments showed that in both cases the drops receded by leaving behind the triple line small droplets with contact angles between 10° and 20° as shown in Fig. 5. The newly exposed surface appears to be darker than the Au layer (see Fig. 5); this leads us to believe that the Au layer has gone from this surface. It should also be noted that the largest drop base diameter attained before receding (roughly 12 mm) is significantly higher than that measured after 20 s of spreading (6.7 mm for $W_{1.2}N$ and 6.1 mm for $W_{1.2}N$). The spreading duration was hence much longer than 20 s.

Figure 6 presents an SEM micrograph of the AuSn20/($W_{1.2}N$/Au) interface taken from the cross-section of the receded drop. It is clearly seen that the Au layer was completely dissolved in the alloy. Inspection with SEM of the substrate surface exposed after receding also proved that the Au layer was consumed. The alloy presents a typical eutectic structure.

As shown by these results, the stoichiometry of the substrates ($W_{1.2}N$ or W_2N) does not influence the wetting behavior by the AuSn20 alloy.

A schematic representation of the spreading process is given in Fig. 7. As it is shown in this figure, the wetting process can be decomposed in several stages.

In the *first spreading stage* ($t < 10^{-2}$ s), the AuSn20 alloy spreads very fast over the Au layer to attain the metastable contact angle of AuSn20 on the solid Au (18°-22°)—*non-reactive wetting*. Indeed, the time needed for small liquid metallic droplets to attain the final contact angle on solid substrates during non-reactive spreading is some tens of milliseconds (Ref 9). The Au layer, having come in contact with liquid alloy AuSn20, starts to dissolve in it by leading, in the vicinity of the interface, to an alloy supersaturated in Au which, in turn, leads to the formation of a 3D compound P rich

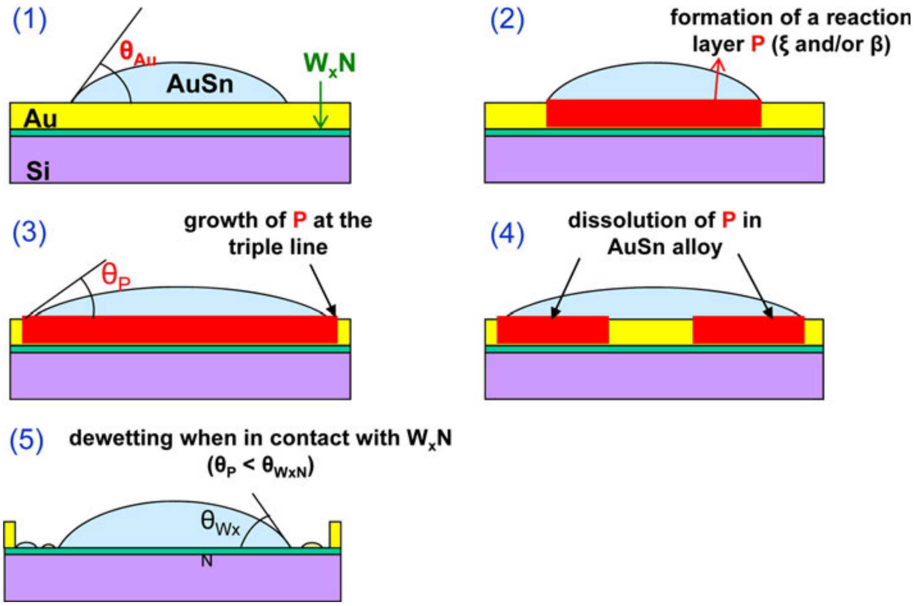

Fig. 7 Schematic representation of spreading and receding of a Au-Sn drop on a W_xN substrate covered by a thin gold layer

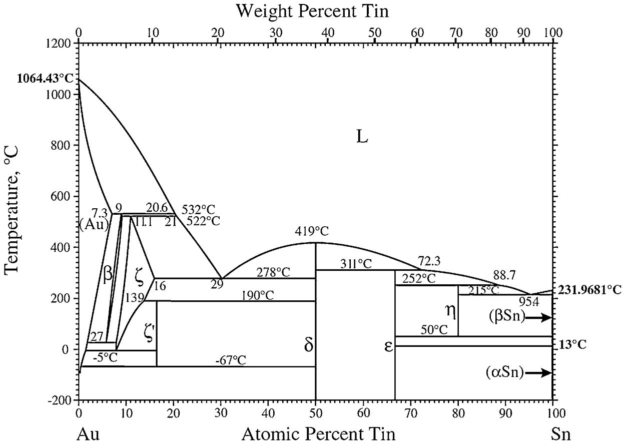

Fig. 8 Phase diagram of the binary Au-Sn system (Ref 10)

in Au. The compounds that can form at 380 °C between the liquid AuSn20 alloy and solid Au are β and/or ξ (see the Au-Sn phase diagram (Ref 10) in Fig. 8).

The equilibrium contact angle of the AuSn20 alloy on the P phase seems to be lower than that on pure Au and the lateral growth of the reaction product P at the triple line lead to a further spreading of the alloy until the equilibrium contact angle is attained on the reaction product P. This *second spreading stage* corresponds to a *reactive wetting* process (spreading time some tens of seconds is several orders of magnitude higher than spreading time corresponding to non-reactive wetting: about 10^{-2} s (Ref 9). In this stage the spreading rate is limited by the rate of formation of the reaction product at the triple line. However, the final equilibrium contact angle on the reaction product P can be attained and remains stable with time only if the reaction product P itself is stable with time, i.e., if the composition of the liquid in contact with P would be that of the liquidus at the considered temperature. From the Au-Sn phase diagram (Fig. 8) it is seen that, at 380 °C, the Au content in the liquid alloy in equilibrium with the ξ compound is 74.2 at.% Au whereas the initial Au content in the alloy is only 71 at.%. Thus, the ξ compound would be stable only if the dissolution of the Au layer is sufficient to increase the Au content in the droplet from 71 to 74.2 at.% and to form the ξ phase of, at least, several nm thick. However, a simple mass balance shows that if even all Au presented in the protective layer is dissolved in the drop of 50 mg it would increase the Au content only from 71 to 72.1 at.%. This last value is significantly lower than that of corresponding to the liquidus of ξ compound (74.2 at.%). Therefore, the ξ compound initially formed at the interface is expected to be in the metastable state and will finally be dissolved in the alloy. The same conclusion would be valid if only the phase β phase or both ξ and β phases are formed at the interface.

Thus, the *third stage* will be the *receding* of the drop until attaining the equilibrium contact angle on the nude W_xN surface. However, it should be noted that receding of the drop will not obligatorily start after the drop attains the equilibrium contact angle on the P compound. Indeed, receding can occur if the rate of formation of the reaction product at the triple line (i.e., the spreading rate), becomes lower than the dissolution rate of the metastable reaction product P at the triple line. A similar dewetting phenomenon was reported and discussed in Ref. 11 in the case of wetting of alumina covered by carbon nanolayers of different thickness by Ni-Si alloys where the receding phenomenon can be accompanied with partial blockings of the triple line leading to successive jumps of this one. This type of phenomenon can be at the origin of formation of several droplets of alloy on the W_xN substrate (see Fig. 5).

3.2 Preliminary Bonding Tests

The bonding tests were performed with two multilayered plates terminating by either $W_{1.2}N$/Au or W_2N/Au. Two cylindrical pieces of the commercial AuSn20 alloy (1 mm long and 500 μm in diameter) were placed between two 15×15 mm^2 plates. No pressure was applied to keep the plates in contact. Such a configuration was heated to 310 °C with a rate of 30°/min in N_2 atmosphere and then maintained for 3 min at this temperature. The cooling rate was also 30 °C/min. Once cooled down to the room temperature the samples were cut perpendicular to the interface for SEM observation.

SEM micrographs of the joint cross-sections of both samples show similar results. The total thickness of the joint in both cases was found to be about 34 ± 2 μm, the alloy presents the typical eutectic structure (similar to that given in Fig. 5) and the Au layer is entirely dissolved in the alloy. The interfaces between the alloy and the tungsten nitride are regular without any pores or cracks. No dewetting phenomena were observed along the interface. Such behavior is consistent with the wetting results presented above. The decrease of the temperature from 380 to 310 °C does not seem to alter the wetting behavior and the 3-min isothermal hold appears to be enough to obtain a good joint and the 100-nm Au layer covering the tungsten nitride serves as a good protection from the oxidation.

4. Conclusions

The wetting behavior of Au-Sn20 alloy in contact with W_xN and W_xN/Au substrates (x = 1, 2, and 2) has been studied at 380 °C under high vacuum. W_xN substrates were found to be covered by a thin oxide layer which remains stable in contact with the alloy thereby preventing good wetting. In contrast, W_xN substrates covered by a thin layer of Au deposited immediately after W_xN deposition appear to be well protected from oxidation. The spreading of AuSn alloy over such substrates was observed to proceed in several steps which, as shown, are strongly related to the complex chemical interaction in the system. After a very fast non-reactive stage, the contact angle measured was found to be about 20°. In the next stage, significantly slower spreading to the contact angle $\theta < 5°$ is attributed to the reactive wetting with formation, at the interface, of metastable Au-Sn compound(s), seemingly being better wetted by the alloy than the Au layer. The consequent dissolution of such a compound resulted in the receding of the triple line accompanied by increasing the contact angle from $\theta < 5°$ to about 25° (presumably, equilibrium contact angle on W_xN). The preliminary bonding tests performed at 310 °C with the W_xN substrates showed that the interface between the Au-Sn20 alloy and the substrates is of good quality, without any cracks and porosity. Similarly to the wetting experiments, the Au layer was found to be completely dissolved in the alloy.

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