Letter

Novel Cu–RuN$_x$ composite layer with good solderability and very low consumption rate

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ABSTRACT

This letter reports a RuN$_x$-bearing Cu layer that has the potential to replace both the wetting layer and the diffusion barrier layer in the conventional under bump metallurgy of flip-chip solder joints. This Cu–RuN$_x$ composite layer was deposited by reactive co-sputtering of Cu and Ru in N$_2$ atmosphere. Experimental characterizations show that Cu–RuN$_x$ exhibits comparable solderability to pure Cu. Most importantly, Cu–RuN$_x$ has a dissolution rate at least one order of magnitude slower than that of pure Cu. A single layer exhibiting these two attributes might offer substantial advantage in cost reduction.

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The under bump metallurgy (UBM) of a flip-chip solder joint serves the key role of establishing a highly reliable linkage between the Si chip and the solder bump. The UBM has to exhibit both proper solderability and sufficient barrier capability against soldering reaction. To meet these two requirements, UBM typically consists of several metal layers, including one metal layer, such as Cu, for solderability (wetting layer), and another layer, such as Ni, for resistance against excessive soldering reaction (barrier layer) [1,2]. An inner adhesion layer, such as Ti, is also commonly used. Such a multi-layer stack inevitably raises cost, and there is a need to reduce the number of layers to a minimum. In other words, it is desirable to find a metal layer that can serve more than one functions. In this letter, an advanced RuN$_x$-bearing Cu layer that has the potential to replace both the wetting layer and the barrier layer is reported.

The detailed procedure for preparing the composite layer of Cu and RuN$_x$ had been reported elsewhere [3], and is omitted here. The Cu–RuN$_x$ composite layer was prepared by co-sputtering Cu (99.999% pure) and Ru (99.99%) targets on (1 0 0) Si wafer in the atmosphere of Ar–10% N$_2$ mixture gas. The overall composition of the film was determined to be 0.4 at.% Ru and 1.7 at.% N (balance Cu) by using secondary ion mass spectroscopy [3]. Bright field transmission electron microscopy analysis [3] showed that the Cu matrix in the Cu–RuN$_x$ composite layer exhibited a columnar structure with an average 10 nm crystallite size (see Fig. 4 of Ref. [3]). X-ray diffraction analysis showed that Ru had reacted with N$_2$ to form a RuN$_x$ compound [3,4].

In addition to this Cu–RuN$_x$ composite layer, experiments were also carried out by using electroplated Cu layer for comparison. For the solderability evaluation, three types of solders, Sn–37Pb, Sn–9Zn and Sn–3Ag–0.5Cu (wt.%) were selected. The solderability was evaluated by measuring the spreading areas of each solder over the Cu–RuN$_x$ composite layer and the electroplated Cu layer. The solder spheres were allowed to spread over the substrates for 20 s at 240 °C, which is a typical peak reflow temperature employed by industry. In this study, the spreading of solder was uniform in all directions, producing spherical cap morphology. Such a uniform spreading is critical to generate reproducible reading of the spreading area. Our experience is that if the substrates are clean, flat, and, most importantly, relatively oxide-free, then the spreading will be quite uniform. Excessive oxide on the substrate is the number one reason for non-uniform spreading. For evaluation on the soldering reaction, the sessile drop method was used. Solder balls of 760 μm in diameter and Sn–3Ag–0.5Cu in composition were placed onto the Cu–RuN$_x$ or Cu substrates, and kept at a constant temperature of 240 °C for different periods of time. The thickness of the dissolved Cu–RuN$_x$ substrate or Cu substrate was determined by measuring the vertical distance between the substrate surface that was covered by solder and the surface that was not covered by solder of the same specimen.

The spreading ratios of the solders on pure Cu and Cu–RuN$_x$ substrates are shown in Fig. 1. The spreading ratio is defined as the

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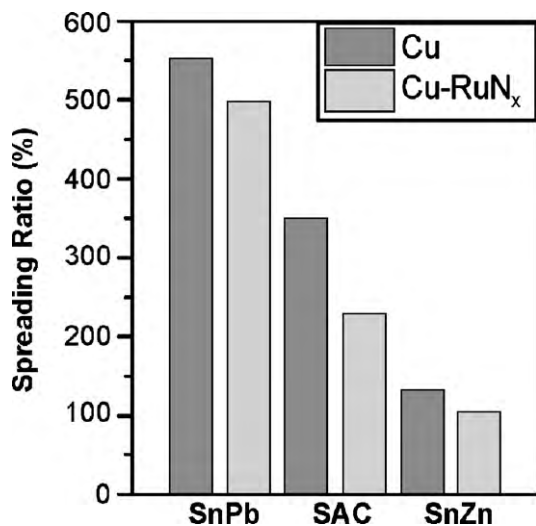 E-mail address: crkao@ntu.edu.tw (C.R. Kao).

Fig. 1. Spreading ratios for Sn–37Pb (SnPb), Sn–3Ag–0.5Cu (SAC), and Sn–9Zn (SnZn) solders over Cu and Cu–RuN$_x$ substrates.

final spreading area divided by the original cross-sectional area of the solder sphere before reflow. A larger spreading ratio in general indicates a better wetting and solderability. As shown in Fig. 1, the Cu–RuN$_x$ layer exhibited a slightly lower, but still comparable, solderability to pure Cu for all three different solders used in this study.

The substrate consumption behaviour during reaction at 240 °C is shown in Fig. 2. The consumption of Cu–RuN$_x$ was at least an order of magnitude slower than that of pure Cu. In fact, this consumption rate was even comparable to that of Ni layer, a diffusion barrier material commonly used in solder joints [5]. The scanning electron micrograph for Cu–RuN$_x$ after 90 s reaction is shown in Fig. 3(a). A thin layer of Cu–RuN$_x$ remained at the interface. Very surprisingly, there was no intermetallic compound of any kind at the interface. In contrast, a thin layer of Cu$_6$Sn$_5$ with the classical scallop morphology formed when the Cu substrate was used, consistently with numerous previous studies on the reaction between Cu and Sn-based solders [2,6–10]. The corresponding X-ray diffraction for the Cu–RuN$_x$ layer after reaction is shown in Fig. 3(b). For this analysis, the solder had been etched away by using an acid solution. Again, no diffraction peak from any intermetallic compound was observed and only peaks from Cu and Cu oxide were detected.
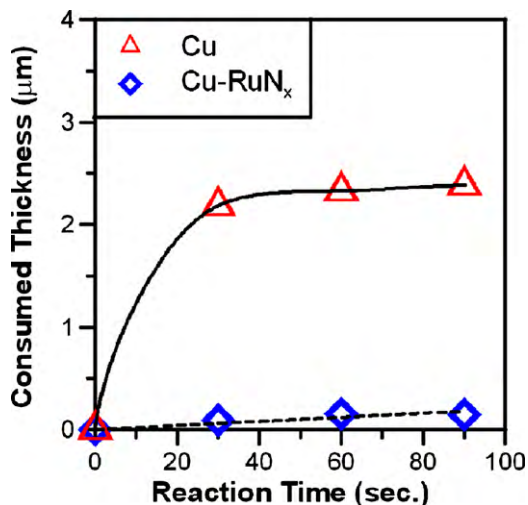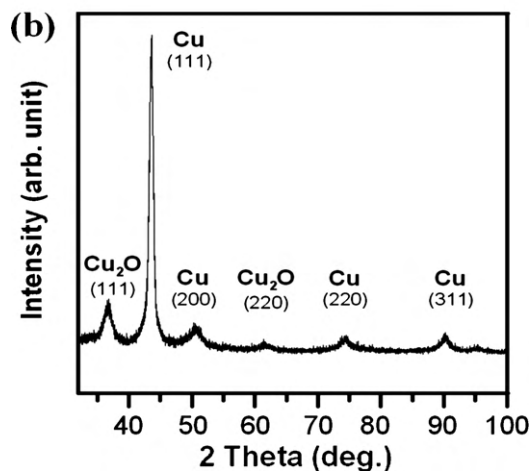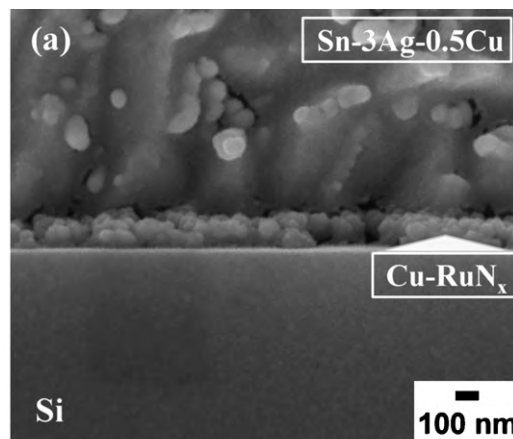

Fig. 3. (a) Electron micrograph showing the Cu–RuN$_x$ substrate after reaction with Sn–3Ag–0.5Cu at 240 °C for 90 s. (b) X-ray diffraction pattern of the interface in (a). The solder was etched away for this analysis.

The Cu oxide probably formed during the solder etching process. The peaks from RuN$_x$ were missing because the weight percentage of RuN$_x$ was simply too small [4]. It was quite interesting that no compound formation between the solder and the Cu–RuN$_x$ layer was observed. In order to clarify this issue, focused ion beam was used to process the cross-section. As shown in Fig. 4, only a thin layer of Cu–RuN$_x$ was observed at the interface, and still no reac-
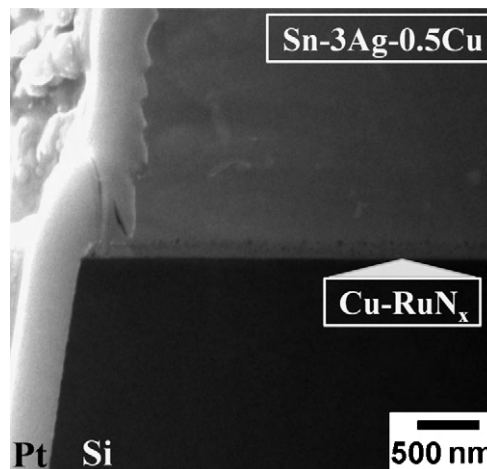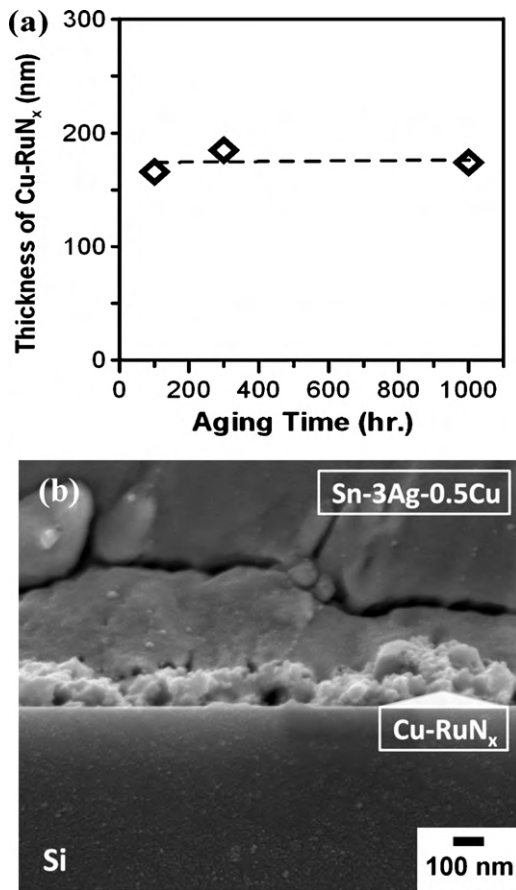

Fig. 2. Consumed thickness of Cu and Cu–RuN$_x$ as a function of reflow time at 240 °C.

Fig. 4. Focused ion beam processed cross-section showing the Sn–3Ag–0.5Cu/Cu–RuN$_x$ interface after reaction at 240 °C for 90 s.

Fig. 5. (a) Thickness of Cu–RuN$_x$ after thermal aging at 200 °C for different periods of time. (b) Electron micrograph showing the Cu–RuN$_x$ substrate after 1000 h thermal aging.

tion product was observed. In addition, no gap between the solder and Cu–RuN$_x$ was observed. It was always possible that a certain reaction product existed but was simply too thin to be resolved by the field emission scanning electron microscope used in this study. Under this situation, the thin reaction product provided the adhesion between the solder and Cu–RuN$_x$. A second possibility was that the reaction product indeed did not form. Under this situation, the adhesion between the solder and Cu–RuN$_x$ was provided by the direct metallic bonds between the solder and Cu–RuN$_x$.

The consumption rate of Cu–RuN$_x$ was also very low during high temperature aging process. As shown in Fig. 5(a), the thick-ness Cu–RuN$_x$ remained almost unchanged even after 1000 h at 200 °C. A resulting interfacial image after 1000 h aging is shown in Fig. 5(b). The Cu–RuN$_x$ layer remained stable, and no intermetallic compound was observed at the interface. It is quite surprising that no reaction product was observed even after such a long period of thermal aging. Moreover, the adhesion between solder and the Cu–RuN$_x$ layer remained excellent. As had been pointed out in a previous study [3], the Cu–RuN$_x$ film had an excellent thermal stability and adhesion to Si, having the capability of withstanding 680 °C annealing for at least 1 h. This seems to suggest that the Cu–RuN$_x$ film is an inherently very stable material. There is no previous report in literature that ally addition to Cu of a few atomic percent is able to completely inhibit the formation of any intermetallic compound at the interface. The exact mechanism for this behaviour is unclear at this moment, and more detailed study is required to resolve this rather novel phenomenon.

In summary, it was demonstrated that the sputter-deposited Cu–RuN$_x$ layer exhibited a very low reactivity with either molten solder or solid solder. The dissolution rate of this layer is as low as that of Ni. No intermetallic compound was observed at the interface with the solder even after long period of solid state aging at 200 °C. In addition, Cu–RuN$_x$ exhibits adequate wetting to solder and has solderability comparable to pure Cu. A single metallisation layer simultaneously exhibiting these two properties has the potential to replace both the wetting layer and the barrier layer, and offers substantial advantage in cost reduction. Uncovering the mechanism for its low reactivity to solders and evaluating the joint strength are two areas that need further investigation.

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References

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