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Effect of surface treatment on adhesion strength between magnetron sputtered copper thin films and alumina substrate

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ABSTRACT

A number of surface pre-treatments have been studied for their effectiveness on the adhesion strength between magnetron sputtered copper (Cu) thin film and polycrystalline alumina (Al_2O_3) substrate. The treatments include organic solvent cleaning, acid washing, heat treatment, plasma cleaning, and they were organized into different sequences in order to evaluate their individual contribution to the film adhesion. Adhesion strength was measured mechanically using a pull test. By proper pre-treatment, the adhesive strength of at least 34 MPa can be achieved with direct sputtering of Cu thin film onto the Al_2O_3 substrate. With the help of XPS, SEM, XRD, TGA and contact angle measurement, the effect of the different substrate surface treatment techniques has been elucidated.

1. Introduction

In the past decades, numerous inorganic (alumina; aluminum nitride etc.) and organic–inorganic materials (polyimide-glass; epoxy-glass etc.) have been utilized as the substrates in electronic devices. In particular, the metallization of ceramics has long been a subject of interest due to its excellent thermal, mechanical and chemical stability, high hardness and good wear resistance [1–5]. This enables the manufacturers to fabricate microelectronic devices with better reliability which are able to work under harsh environment. In order to fully achieve the advantages, good adhesion between the metallization films and the substrate is crucial. However, since metals tend to have a higher surface energy than ceramics, it is difficult to form a strong bond between metal films and ceramic substrate.

An electronic package usually consists of different materials for different functions which are often connected via physical and/or chemical means. Debonding or delamination between these heterogeneous materials during fabrication or service is always of a great concern for device reliability. Metallization on ceramic substrates is an important issue due to the intrinsic low adhesion caused by poor wetting of metals on ceramics. MIL-STD-883E standard (method 2027.2) [6] requires a minimum of 10 MPa for metallization on ceramic substrate. To achieve the desired adhesion strength, many factors have to be considered to develop a better bonding between different materials. In the study of joining method, various techniques such as eutectic joining [4,5,7–10], ion beam dynamic mixing [11], casting bonding [7], spraying [12,13], etc., have been explored to obtain optimized bonding. Besides, insertion of an adhesion layer such as titanium [14], chromium [14,15] or tantalum is often employed before the final metal film is deposited on a ceramic substrate. These methods either require a high processing temperature, or additional materials and steps.

There is a clear advantage to form metal films on a ceramic substrate without using an adhesion layer. In such a case, the surface condition is an important factor that affects the bonding strength. It is well known that a clean surface is very important to achieve high adhesion strength. Over the years, a variety of surface treatment methods have also been extensively developed for improving interface adhesion. However, the topic related to the impact of surface pre-treatments to the Cu–polycrystalline Al_2O_3 bonding has not been systematically studied and little has been known for the effectiveness of individual surface treatment as many reports were focused on an optimum solution. In this paper, effort has been made to increase the adhesive strength between Cu thin film and polycrystalline Al_2O_3 by employing a few types of surface treatment prior to bonding as listed in Table 1. Copper thin films of

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Table 1
Types of surface pre-treatments, group into different sequences, and the resulting adhesion strength.

Treatment	Cleaning steps	Description	Average adhesion strength (MPa)
Group 0	No	As-received sample	5.4 ± 3.4
Group 1	Solvent cleaning	Acetone 10 min with ultrasonication IPA 10 min with ultrasonication Dry at 70 °C for 3 min	6.1 ± 1.7
Group 2	Solvent cleaning → Acid etching	Solvent cleaning as described above Piranha acid at 90 °C for 15 min Rinse with distilled water Dry at 70 °C for 3 min	7.1 ± 1.9
	Solvent cleaning → Heat treatment	Solvent cleaning as described above In situ heating at 300 °C for 30 min right before film deposition	7.3 ± 1.8
	Solvent cleaning → Plasma treatment	Solvent cleaning as described above In situ Ar plasma treatment at 50 W a) 2 min b) 10 min	2 min: 25.0 ± 6.0 10 min: >34.0
Group 3	Solvent cleaning → Heat treatment → Plasma treatment	Solvent cleaning as described above In situ heating at 300 °C for 30 min In situ Ar plasma at 50 W for 2 min	16.9 ± 3.0
	Solvent cleaning → Plasma treatment → Heat treatment	Solvent cleaning as described above In situ Ar plasma at 50 W for 2 min In situ heating at 300 °C 30 min	5.3 ± 2.1
Group 4	Solvent cleaning → Plasma treatment → Re-contamination	Solvent cleaning as described above In situ Ar plasma at 50 W for 10 min Exposed to air at mosphere for 10 days	7.7 ± 7.0

around 1.0 ± 0.2 μm were sputtered on polycrystalline Al_2O_3 substrate without employing any adhesion layer. Different surface treatments are designed to be applied in different sequences to understand the contribution by each of these treatments. Adhesion between Cu film and the Al_2O_3 substrate was examined by a tensile test. Scanning electron microscope (SEM) was used to examine the surface morphology. The level of surface cleanliness was investigated using X-ray photoelectron spectroscopy (XPS). In addition, surface energy was measured before and after the treatment using the contact angle method to understand its quantitative variation.

2. Materials and methods

2.1. Sample preparation

Polycrystalline Al_2O_3 substrates with purity of 96% were purchased from Semiconductor Wafer, Inc., Taiwan. The substrates were first diced with the dimension of $3.0 \times 3.0 \times 0.6\,mm^3$ using a diamond blade by DISCO DFD 6361 fully automated dice saw, at the speed of 1.0 mm/s. Before film deposition, the substrates were cleaned using different combinations of treatment as listed in Table 1.

Immediately after the surface treatment, Cu thin film was deposited onto the Al_2O_3 substrate using DC magnetron sputtering technique (PRO Line PVD 75, Kurt J. Lesker Company®). The sputtering chamber was pumped to a vacuum level below 5.0×10^{-5} Torr before the coating process starts. After the desired vacuum pressure was reached, the deposition will be conducted under the power of 300 W with deposition pressure of 1.5×10^{-2} Torr with Ar gas, and the deposition rate was about 0.3 nm/s. During the deposition, the sample holder was rotated at 20.0 mm/s in order to obtain a uniform film. The distance between the substrate holder and the sputtering target was maintained at 20.0 cm.

A comparison study was also conducted using monocrystalline Al_2O_3 substrate (Latech Scientific Supply Pte Ltd, Singapore) with surface roughness (root mean square, *rms*) less than 0.5 nm. The purchased monocrystalline substrate in the orientation of $(1\,1\,\bar{2}\,0)$ has similar surface energy with polycrystalline Al_2O_3 substrate. Surface analysis after treatment was investigated and compared based on the density of substrate surface pores.

2.2. Materials characterization and adhesion measurement

Investigation on the substrate's chemical state on the surface and subsurface (depth profiling) was carried out by a Kratos Axis Ultra X-ray photoelectron spectroscopy system under the vacuum state of 10^{-8}–10^{-9}. The binding energies of the elements were calibrated using CASA XPS processing software by referring the adventitious C 1s peak at 284.8 eV as internal reference. The surface energy of the substrate was measured using three different liquids: viz. distilled water, ethylene glycol and diethylene glycol with known surface energy. The surface energy of the ceramic samples was then calculated using the Owen, Wendt, Rabel and Kaelble (OWRK) method. X-ray diffractometer (Shimadzu, Japan) equipped with a secondary monochromator with Cu Kα radiation was used to determine the crystal structure of the substrate in the scan range from 20° to 80°. The amount of solvent residue was measured using a thermal gravimetric analyser (TGA-Q500) under a controlled atmosphere.

The adhesion strength between the film and substrate was measured using a mechanical tester (Instron 5567) with a load cell of 500 N. A superglue (Selleys Supa Glue, Australia) was applied to adhere the Cu film to a test fixture. The mechanical pull test with a loading speed of 10.0 μm/s was carried out under ambient condition. The bonding strength is calculated as the average tensile stress at failure. The reported strength was an average value from 10 pieces of test specimens. The separated surfaces were then analyzed using scanning electron microscopy JEOL JSM 6360 to examine the location of the failure. True adhesion strength was available only if the failure is between the Cu film and the Al_2O_3 substrate. If cohesive failure in the applied glue or adhesive failure between the glue and the Cu film is observed, the case will be