Suppression of de-wetting of copper coatings on carbon substrates by metal (Cr, Mo, Ti) doped boron interlayers

D. Schäfer a, J. Hella,*, C. Eisenmenger-Sittner a, E. Neubauer b, H. Hutter c, N. Kornfeind c

a Vienna University of Technology, Institute of Solid State Physics, Wiedner Hauptstraße 8-10, A-1040 Vienna, Austria
b Austrian Research Centers GmbH-ARC, A-2444 Seibersdorf, Austria
c Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9, A-1060 Wien, Austria

Keywords:
- Wetting
- De-wetting
- Copper–carbon system
- Metal doped boron interlayer
- Sputter deposition

A B S T R A C T

Boron coatings doped with Cr, Ti or Mo were deposited on plane substrates of vitreous carbon ("Sigradur G") by magnetron sputtering from a composite target. The amount of included metal was determined by Auger electron spectroscopy and found to be in the range of 1–4 at%. The metal content relative to boron was chosen to be in the range of 3 at% for all interlayers. Onto these interlayers a Cu film of 300 nm thickness was deposited by magnetron sputtering. After that the Cu coated samples were subjected to heat treatment of 800 °C for 30 min.

The heat treated samples were investigated by scanning electron microscopy and time of flight secondary ion mass spectroscopy (TOF-SIMS). Different intensities of de-wetting of the Cu coatings could be observed. It was possible to quantify the de-wetting process by determining the area density of holes formed within the Cu coating after thermal treatment. Interlayers which lead to the lowest hole density will be considered as candidate materials for optimizing the thermal properties of the Cu/C interface in subsequent experiments.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Novel heat sink materials consist of a highly thermal conductive matrix, e. g. copper with equally thermal conductive inclusions (e.g. carbon fibres, nanotubes or diamond particles). These inclusions allow for a reduction of the high coefficient of thermal expansion (CTE) of copper (CTE copper: 16 ppm/K, various C modifications: approx. 2 ppm/K). The thermodynamic immiscibility of Cu and C [1] leads to a high thermal contact resistance (TCR) between matrix and inclusion. To overcome the problem of insufficient thermal transport across the Cu/C interface wetting promoting interlayers may be a solution. One candidate material for these interlayers is metal doped boron.

2. Experimental

All metal doped B interlayers were deposited on glassy carbon substrates by RF – magnetron sputter deposition from a composite target at an average pressure of 0.4 Pa and a discharge power of 100 W at room temperature (RT). The working gas was chosen to be either argon, nitrogen or a 50% N2 50% Ar mixture. The deposition rate was approximately 0.16 nm/s irrespective of the working gas. The layer thicknesses were chosen to be 5 nm, 30 nm and 100 nm.

The composite target was built by placing chromium, titanium or molybdenum pieces on a sintered boron target of 50 mm diameter. With the known sputter yields of the metals [2], calculations of how much area those pieces had to cover to achieve compositions of 1–4 at% were performed. Experimentally the amount of metal in B was determined by Auger electron spectroscopy. For this measurement the composite material was deposited on a silicon-wafer in order to avoid carbon impurities. The metal concentration was found to be in the range of 1–4 at% as previously calculated.

For all further investigations first the metal doped interlayers were deposited on glassy carbon substrates and then covered by a 300 nm Cu coating which was deposited by DC magnetron sputter deposition with a deposition rate of approximately 2 nm/s. In this case Ar at a pressure of 0.4 Pa was used as working gas and the discharge power was 200 W, the deposition temperature was RT.

After the deposition procedure the samples were subjected to a heat treatment of 800 °C for 30 min under high vacuum conditions.
3. Results and discussions

All samples were investigated by scanning electron microscopy (SEM). As one can see in Fig. 1 the heat treatment results in the formation of holes all over the sample. The mechanism of hole formation is described elsewhere [3,4]. As the number and area of the holes varied from sample to sample, this might be an indicator for the de-wetting process. An image processing program (UTHSCSA Image Tool Version 1.28) was used to count the number of holes on the sample and to determine the mean area of the holes. By multiplying the number of holes and their mean area the whole uncovered area of the sample was specified. This number can be taken as a measure for the suppression of de-wetting with low values indicating good wetting properties. Figs. 2 and 3 show an overview of these values for the B and B–Mo interlayer material combined with interdiffusion in the film-stack result in a lower wettability compared to coatings deposited with Ar as working gas. Therefore samples produced with N2 or N2/Ar were discarded for further investigations.

To study the influence of heat treatment on the interdiffusion of the various materials within the samples TOF–SIMS measurements on untreated and heat treated samples were performed. Fig. 4a and b show this comparison for Cr doped interlayers. All other interlayers exhibited similar behaviour. Diffusion of the interlayer material into the Cu coating can only be observed for the heat treated samples. Especially in the case of Cr one can see that Cr diffuses to the surface while B does not. This could indicate that there is no chemical bonding between B and the doping material.

In addition pull-off tests were performed to investigate the adhesion strength of the Cu coating which is another indicator for the wetting/de-wetting process. The SEM-investigations showed that interlayers with a thickness of 5 nm complied best with the requirements for a suitable wetting promoting layer (minimum total hole area). In the case of the 5 nm B–Cr interlayer the uncovered area is 0.6% whereas it is 1.3% at a thickness of 100 nm. As this result was similar for all investigated interlayer types, only samples with 5 nm interlayers were analysed via pull-off tests, performed on at least 4 samples. For the nonheat treated samples, the results are very clear, as one can see in Fig. 5.

For all coatings deposited with N2 and the N2/Ar mixture as working gas, the total uncovered area was much higher than with Ar alone. Probably chemical reactions of N2 with the coating material combined with interdiffusion in the film-stack result in a lower wettability compared to coatings deposited with Ar as working gas. Therefore samples produced with N2 or N2/Ar were discarded for further investigations.

The results change for the heat treated samples. While the B–Cr and the B–Mo interlayer with an adhesion strength of about 579 N/cm² was found while the B–Cr interlayer for example only shows a value of 377 N/cm². Compared to the Cu coating without any interlayer (364 N/cm²), the B–Mo interlayer as the best of all investigated samples provides an increase of about 59%.

The results change for the heat treated samples. While the B–Cr and the B–Mo interlayer with an adhesion strength of about 579 N/cm² show very similar behaviour, the value for the B–Ti interlayer is 110 N/cm². Comparing these results with the value for the Cu coating without any interlayer (162 N/cm²) the B–Cr and the B–Mo interlayer provide an increase in adhesion strength of about 55%. The B–Ti interlayer shows a significant decrease of adhesion strength when comparing the heat treated sample to the untreated one. The adhesion strength of the heat treated B–Ti samples is even lower than the adhesion strength of heat treated samples without any interlayer.

**Fig. 1.** SEM image of 300 nm Cu on 5 nm Cr doped B interlayer, working gas: N2; bright areas: Cu coating, dark areas: holes.

**Fig. 2.** Comparison of the uncovered area on samples with B and Mo doped B interlayer with no interlayer for three different working gases.

**Fig. 3.** Comparison of the uncovered area on samples with Cr and Ti doped B interlayer with no interlayer for three different working gases.
4. Conclusion and outlook

The determination of the total uncovered area in Cu coatings deposited on metal doped B films is a suitable tool for the determination of wettability. This tool in combination with the SEM-investigations showed that N₂ and the N₂/Ar mixture as working gas will not lead to the demanded wettability increase. Thin interlayers (5 and 30 nm) deposited with Ar as working gas are the most promising candidates for wetting promotion. Pull-off tests on these samples identified Mo as the most adhesion promoting doping material for the B interlayer.

Further research will assume that adhesion strength and wettability are connected to thermal conductivity [5]. Diamond substrates, covered with these optimum interlayers, will be used instead of the glassy carbon, because the main focus in the future will be on the optimization of the interlayer in diamond–copper systems.

Acknowledgement

The financial support of the Austrian FWF “Fonds zur Förderung der wissenschaftlichen Forschung” Grant No. P-19379, is gratefully acknowledged.

References