Characterisation of molybdenum intermediate layers in Cu–C system with SIMS method

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Available online 22 April 2005

Abstract

In the design of new high-speed chip generations a huge problem is bleeding off process heat during their operation. The installation of heat sinks onto such chips is necessary. Possible materials are copper-coated carbon composites. They combine high thermal conductivity with low density and a tailorable coefficient of thermal expansion (CTE). The low wettability of copper onto carbon necessitates a surface pretreatment.

Flat slices of nitrogen-plasma etched vitreous carbon (Sigradur G) made up as a model system for carbon fiber material. The later serial fabrication of these fibers includes a hot pressing step after the deposition joining them to solid composites. It is simulated by a heat treatment step of the compound. The first sample series consisted of samples with 100 nm molybdenum and 500 nm copper layers (sputter deposited), as deposited and heat treated. The second run concludes samples without molybdenum layer but an additional 50 nm cap layer deposited after heat treatment.

All samples were investigated with secondary ion mass spectrometry (SIMS), showing a diffusion of carbon into the molybdenum layer. Measuring MCs + secondary ions, both matrix elements and trace elements were detectable sufficiently.

PACS: 82.80.Ms

Keywords: SIMS; Sputter deposition; Heat drain; Molybdenum; Molybdenum carbide

1. Introduction

Efficient cooling techniques are needed. In addition to geometric optimization, there is a parallel push toward the research of novel heat conducting material.

One among these is a metal–matrix-composite system (MMC), a material class with tunable mechanical and thermal properties, which can be used in applications where the matching of thermomechanical characteristics is crucial. They are able to combine properties of a metallic matrix and the...
physical advantages of a reinforcement material. Latter can rely either on particles or on fibers.

Copper-coated carbon fibers are a good example for composites of this material class. Such fibers combine high thermal conductivity with low density and a tailorable CTE in order to match it to standard electronic materials such as silicon while retaining the high thermal conductivity of copper for heat removal.

A low wettability of copper onto polycrystalline carbon [1] necessitates a bond strengthening surface pretreatment. Examples for reactive intermediate layers forming carbides such as Cr and V are reported in [2,3].

But a further heat treatment step compacting the fibers to solid slices weakens the joining. Former SIMS investigations on chromium intermediate layers [4,5] have shown a diffusion of chromium onto the surface, and a de-wetting of the interface area. Further tested vanadium and titan also failed after heat treatment [6]. More successful were investigations with a molybdenum interface, where AFM and Auger studies have shown no de-wetting [7]. The adhesion strength is also increased after heat treatment [8].

This work centers a comparison of the molybdenum and carbon distribution before and after heat treatment investigated with the SIMS method. It is split into two parts:

- In a first run samples were deposited with molybdenum and copper (similar to [7]) and analyzed as deposited and heat treated (see also Section 3.1).
- In a second run samples without copper facing were investigated, also as deposited and heat treated. A second molybdenum layer was deposited after heat treatment. This cap layer should decrease effects from matrix influences, preferential sputtering and enhanced sputter rate (see also Section 3.2).

## 2. Experimental

Like former studies [4–9] glassy carbon substrates (SIGRADUR G, [10,11]) were used to model carbon fibre material. Before the first deposition the substrates were degreased by ultrasonic cleaning in acetone and ethanol followed by vapour phase cleaning in ethanol vapour and then stored at 80 °C until the insertion into the deposition chamber to guarantee a dry surface.

All layers were PVD-deposited using an ALCAT-EL SCM450. Deposition equipment parameters are similar to former investigations [6–8,12]. Deposition parameters like sputter rate and layer thickness are listed in Table 1.

The first batch consists of the samples 1A and 1B. They were deposited together; both layers (100 nm molybdenum and 500 nm copper) in a row. After deposition sample 1B was taken to a heat treatment at 800 °C for 1 h under high vacuum (see also description in Table 1).

The second batch (samples 2A and 2B) consists of samples only with molybdenum layers. At first, a molybdenum layer was deposited onto each substrate (see Table 1). Then all samples were removed from the vacuum and stored under air without special precautions. Sample 2B was heat treated similar to sample 1B (Table 1). At last ahead to SIMS measurements a second molybdenum layer was deposited onto both samples.

SIMS measurements were carried out with a CAMECA IMS 3f using Cs+ primary ions with 5.5 keV effective acceleration. Ion current for samples 1A and 1B was 100 nA, for second batch samples (2A and 2B) 15 nA. We decided to detect positive secondary ions mostly measuring MCs+ ions. This detection mode allows the measurement of ions with reduced matrix influence [13,14]. Anyhow a change of the signal intensity might not correlate with a change

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molybdenum deposition (nm) (rate: 0.5 nm s(^{-1}))</th>
<th>Copper deposition (nm) (rate: 1.5 nm s(^{-1}))</th>
<th>Molybdenum cap layer deposition (nm) (rate: 0.5 nm s(^{-1}))</th>
<th>Heat treatment (800 °C, 60 min, high vacuum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>100</td>
<td>500</td>
<td>–</td>
<td>No</td>
</tr>
<tr>
<td>1B</td>
<td>100</td>
<td>500</td>
<td>–</td>
<td>Yes</td>
</tr>
<tr>
<td>2A</td>
<td>100</td>
<td>–</td>
<td>50</td>
<td>No</td>
</tr>
<tr>
<td>2B</td>
<td>50</td>
<td>–</td>
<td>50</td>
<td>Yes</td>
</tr>
</tbody>
</table>
of the composition, so only a comparison layer by layer is valid.

The depth scale from SIMS raw data is highly distorted due to discrepancies in the sputter rate of each matrix. We decided to adjust it with sputter yield data obtained from SRIM simulations [15]. Input data for sputtered material were for each layer a mixture of main element and cesium. The cesium amount at the surface was chosen in a way to obtain a sputter yield of $Y = 1$ for cesium (when impact equals emission). The obtained sputter yield data (see Table 2) were converted into sputter rate and adjusted to the depth profiles. The change of layer and, therefore, of the sputter rate was manually set leading to a roughly adjustment of the depth scale.

Additional depth measurements of the sputter crater adjusted the profile end. These measurements were done using a SLOAN DECTAC IIA profilometer.

Due to a lack of standards we were not able to quantify the samples. We assume a purity of at least 99% for all layers. So the rest (e.g. oxygen and nitrogen) sums up to below 1%.

3. Results

3.1. Samples 1A and 1B (including a copper layer)

Fig. 1 shows signals of selected masses from depth profiles of samples 1A (dotted lines) and 1B (solid lines). Two vertical, dotted lines at approximately 0.45 and 0.6 μm indicate the Cu/Mo and Mo/C interfaces.

Copper diffuses a little bit into the carbon substrate during heat treatment, but within the upper layers there is no significant difference between samples with and without heat treatment. The molybdenum peak becomes smaller, but broadens. The former one indicates a decrease of the molybdenum concentration. The latter one may indicate a broadening due to

Table 2
Simulated sputter rate of several matrices using SRIM 2003

<table>
<thead>
<tr>
<th>Element</th>
<th>Sputter rate (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>11</td>
</tr>
<tr>
<td>C</td>
<td>5.5</td>
</tr>
<tr>
<td>Mo</td>
<td>2.6</td>
</tr>
<tr>
<td>Mo (in Mo$_2$C)</td>
<td>3</td>
</tr>
</tbody>
</table>

![Image](image.png)

![Image](image.png)
diffusion, but this effect may also originate from a rougher interface. With available SIMS data we are not able to state this. The carbon distribution changes drastically by diffusion of carbon into the molybdenum layer caused by tempering. Investigations on carbide layer growth in similar systems [16,17] affirm the formation of Mo2C after heating to 800 °C. The diffusion coefficient in these papers differs for about 2 powers of magnitude. Nevertheless both values describe the changes in our nm-scale system sufficiently. Both molybdenum and carbon arise parallel at the Cu/Mo interface in sample 1B (after heat treatment; continuous lines in Fig. 1), indicating that there is no metallic molybdenum remaining.

In addition some trace elements were measured. High amounts of elements like sodium, potassium, calcium at the Mo/C interface are relics from the surface contamination (not shown in this paper). In sample 1A oxygen is present at both interfaces, whereas in sample 1B (after heat treatment) it is enriched at the Mo/C interface. Nitrogen decreases in the copper layer significantly from sample 1A to 1B. This element is probably a contaminant of the sputter gas and gases out during heat treatment. The amount remaining in the transformed Mo2C layer is probably a nitride formation as known from most refractive metals.

3.2. Samples 2A and 2B (molybdenum cap layer)

Fig. 2 shows a comparison of the depth profiles of samples 2A and 2B. Here, the copper cover layer is replaced by a thin molybdenum layer of 50 nm, which is deposited after a longer storage at the atmosphere. This cap layer thickness was chosen in a way to inhibit effects from preferential sputtering and enhanced near surface sputter rate. It also reduces effects from changes of the matrix due to the use of the equal element in this top layer (though Mo2C and metallic Mo still differ in their matrix influences). So it is possible quantify the signal drop of molybdenum with ~40%.

The thickness of the second (first deposited) molybdenum layer differs at both samples. At sample 2A 100 nm molybdenum was deposited, whereas at sample 2B it was only 50 nm. This and additional changes of the sputter rate cause a variation of the Mo/C interface location in these depth profiles.

Like in sample 1A and 1B the carbon signal increases after heat treatment in the molybdenum
layer (the heat treatment was performed before deposition of the upper molybdenum layer!). But due to the reduced sputter rate of these profiles some details are visible in these depth profiles.

A light increase of carbon in sample 2A (not heat treated) toward the Mo/C interface (pointed up in Fig. 2 with an increasing line). Two effects may cause this: a weak diffusion at room temperature or pinholes in the layer. Intended TEM measurements may clear up this.

The signal of nitrogen drops after heat treatment within the molybdenum layer. The change of the light signal of oxygen in samples 1A and 1B is not observable in these samples.

4. Summary and conclusion

SIMS measurements of molybdenum layers were done as part of studies focusing on their capability as adhesion promoting intermediate layer for bonding copper onto carbon substrates. Samples with and without heat treatment as well as samples with copper layers and samples with specially prepared molybdenum cap layers were investigated with SIMS detecting MCs ions. We found in all heat treated samples carbon increased within the molybdenum layer. Molybdenum is most probably changed into carbide. From investigations on thicker samples this layer was confirmed to be Mo_2C by X-ray diffraction measurements [17]. We did not find any diffusion of molybdenum through the copper layer. This is affirmed by auger investigations [7] and shows the advantage of molybdenum in comparison to all other elements tested so far. SIMS investigations on chromium layers in similar systems [4,5] show huge amounts of chromium diffusion to the surface. Unlike molybdenum chromium also diffuses through the copper layer. This makes molybdenum more calculable and more suitable as intermediate layer.

Although there are huge changes in the molybdenum layer during heat treatment, an increase in bond strength was observed in former studies [7]. This may result from interface roughening observable in SIMS depth profiles as smoothing of the carbon and molybdenum signal’s slope.

Acknowledgment

This work was supported by the Austrian Scientific ‘Fonds zur Förderung Wissenschaftlicher Forschung’ (grant P 15931-N03).

References