Interface resistance in copper coated carbon determined by frequency dependent photothermal radiometry

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Abstract. The heat transfer in copper-carbon flat model systems was studied by frequency dependent photothermal radiometry. A novel approach which relies on the frequency dependence of the photothermal signal phase and amplitude at intermediate frequencies was introduced to determine the thermal interface resistance between the Cu-film and the substrate. The frequency dependent amplitude and phase of the photothermal signals were analyzed in the frame of a model of a one-dimensional heat flow perpendicular to the film plane. The interface resistance of the investigated CuC-sample with a Ti-bonding layer was found to increase by a factor two on heat treatment.

1. Introduction
Thermal interface resistance $R_i$ is a key property for protection coatings and for nano-composite materials as it governs the heat transport across the interface. Applying a heat flux density $dq/dt$, $R_i$ creates a temperature drop $\Delta T_i$ across the interface between coating and substrate: $\Delta T_i = (dq/dt)R_i$. A finite temperature drop at the interface also exists for an ideal mechanical and chemical contact. This intrinsic interface resistance called Kapitza or boundary resistance results from the scatter of the “heat particles” (phonons, electrons) at the boundary due to the discontinuous change of the physical properties at the boundary [1]. Theoretical estimates of the boundary resistance were obtained in the frame of models based on coherent and diffuse phonon scattering mechanisms [2,3]. All theoretical and experimental studies of solid-solid interfaces point towards a boundary resistance at room temperature which is typically of the order of $10^{-8}$ m$^2$KW$^{-1}$ [2,4,5]. With decreasing temperature when the mean free path of the phonons and electrons becomes larger the boundary resistance is found to increase by a $T^{-3}$-law [2]. For a non-ideal mechanical or chemical contact of coating and substrate an additional contact resistance can appear which may be due to air voids or chemical induced contact layers with a lower thermal conductivity than the coating or substrate. This contact resistance governs the heat transport across the interface in composites which are produced by pressing or by gluing. The contact resistance exhibits a smaller temperature dependence and changes upon pressure [6].

This work is devoted to the investigation by frequency dependent photothermal radiometry (PTR) of the interface thermal resistance of Cu-films with thicknesses about 1 micron and less deposited on a carbon substrate. Although a Cu-layer of this thickness can only be resolved at MHz frequencies we
shall demonstrate that reliable information on the interface resistance between layer and substrate can already be retrieved at much lower modulation frequencies. With respect to the flash techniques commonly used in the case of very thin films [5] the present approach based on the frequency domain IR radiometry provides a means to study interface resistance of films of thicknesses in the one micron range.

2. Experimental
The samples are based on a flat substrate of amorphous carbon covered with Cu-layer and a bond layer in-between. Many modification strategies were applied, e.g. ultrasonic cleaning, plasma treatment, and introducing intermediate bond layers, in order to improve the adhesion strength and to reduce the thermal contact resistance at the interface. The Cu-films and intermediate bond layers of different thicknesses were deposited by CVD process. The thickness of the carbon substrate was 5 mm and that of the Cu-film 800 nm. The bonding layer of Ti or Cr varied between a couple of nanometers up to 100 nm. In addition, after the deposition of the Cu-films and bonding layers, part of the samples were treated thermally by an annealing process at 800 °C in order to simulate the consolidation process during the fabrication of Cu-C composites. To analyze the effects of the different preparation processes with respect to the consolidation process of copper-carbon composites, the samples were measured before heat treatment and after heat treatment.

![Figure 1 Set-up for the modulated photothermal IR-radiometry (PTR) measurements.](image)

To determine the thermal interface resistance between the Cu-layer and the carbon substrate as a function of different treatments of the substrate and of the bonding layer, experiments of modulated PTR have been conducted. The samples were heated by a laser at wavelength of 514 nm. The modulated IR-signal from the Cu-surface was measured by a MCT-detector at modulation frequencies ranging from $f=10$ Hz to 100 kHz (Fig. 1). All measurements were performed at room temperature.

3. Theoretical considerations
The PTR data were analyzed in the frame of a one-dimensional model system consisting of a film of thickness $d$ and thermal conductivity $k_f$ on glassy carbon (Sigradur) substrate of thickness $D$, with an interface resistance $R_i$ and air-backing. The bonding layer is included in the interface resistance.

When solving the heat diffusion equation at the interface between coating and substrate, instead of the continuity of temperature $T_i(z_i = d) = T_2(z_2 = d)$, a finite temperature step determined by a thermal resistance is taken into account: $R_i = - \frac{T_i(d) - T_2(d)}{k_i \left( \frac{\partial T_i}{\partial z} \right)}$. 


Fig. 2 shows the simulations of the frequency dependence for the normalized phase of the surface temperature using thermal parameters of Cu and Sigradur from literature. Normalization is made with the surface temperature of Sigradur as reference. The phase of the surface temperature shows a minimum at high frequencies as expected for a two layer system. For a 0.8 µm Cu-film on Sigradur this minimum appears at about 7 MHz. The magnitude of the phase shift at minimum is governed by the ratio $\frac{e_s}{e_b}$, where $e_s$ is the effusivity of surface layer and $e_b$ that of the substrate [7]. With increasing $R_i$ this minimum gets more pronounced. Physically, the reflection of the thermal wave at the interface is increased by the interface resistance. Although the phase extremum provides all necessary information on $R_i$, due to its situation at high frequency it is not accessible experimentally by IR-radiometry. However, the presence of $R_i$ leads also to deviation of the phase behavior at lower modulation frequencies (indicated by the bar in Fig.2) which are in the frequency range of conventional PTR experiments. Here, finite $R_i$ values cause smaller phase shifts (broken lines) than those expected for a two layer system without interface resistance (solid line). The physical reason for that is the superposition of the incoming and the reflected thermal waves, which is more pronounced if $R_i$ has a finite value. In the frequency range up to 100 kHz the PTR signal is proportional to the normalized thermal impedance $z_n$ of the layered system and is expressed approximately as:

$$z_n = 1 - \left( \frac{b_{sb}}{1-i} \right) R_i - R_s \left/ z_b \right.$$ 

with $R_s = d/k_s$ the thermal resistance of the surface layer and $z_b = (1-i)/(4\pi f)^{1/2} e_b$ the thermal impedance of the substrate [8].

4. Experimental results and discussion

In the course of the project mentioned in the Acknowledgements a large number of flat samples have been measured and analysed. Distinct variations of the interface resistance with sample treatment and bonding layers have been observed. The data of all measurements and details of the observed correlations will be published elsewhere. In this contribution we shall restrict to the effect of the heat treatment on the interface resistance of one CuC-sample in order to demonstrate the power of the experimental method for the study of interface resistance. The example also unveils the main disadvantages connected with the thermal wave approach. In Fig.3 the phases obtained from an as-prepared and heat treated Cu(800nm)/Ti(20nm)/C(5mm) sample are compared with the results of simulations calculated for different interface resistances. The heat treatment, performed at about 800°C in vacuum, clearly increases the interface resistance by about a factor of two. However, the absolute values of $R_i$ deduced from the frequency dependence of the phase lag depend on the used thermal parameters of the Cu-film and of the C-substrate for the fitting procedure. Whereas the influence of the thermal conductivity values of the Cu-film is small, the values of the mass-density of Cu-film and that of the Cu-film thickness have a large impact on the result. A reduction of the mass-
density of the Cu-film by 20% reduces the interface resistance by about 40%. Nevertheless, the relative change between the as-prepared and heat treated samples remains constant. Similar results are found for a variation of the thickness of the Cu-film.

Another aspect concerns the resolution of the interface resistance changes. For the sample system Cu-C studied in this work, $R_i$ values below $10^{-8}$ m²K/W can hardly be resolved (see theoretical curves in Fig.3). This is essentially due to the low thermal conductivity of the carbon substrate.

5. Conclusions
Using the photo-thermally modulated IR radiometry the thermal transport properties at the copper-carbon interface were investigated. The photothermal technique provides simultaneously indirect information on the contact and on the adhesion between the different constituents. A new approach is presented which allows one to determine the interface thermal resistance between a thin metallic layer and the lower conducting substrate. This can be achieved by PTR already at kHz frequencies corresponding to ms time regime. As for other thermal wave based techniques the absolute values of the thermal interface resistance strongly depend on the thickness and on the mass-density of the metal film. Detailed model simulations for the Cu-C systems under investigation, indicate that the contrast for the determination of the interface thermal resistance decreases considerably with decreasing resistance as a consequence of the low thermal conductivity of the carbon substrate.

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