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Thermal boundary conductance between refractory metal carbides and diamond

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Abstract

The thermal boundary conductance (TBC) between thin films of Cr, Mo, Nb and W and diamond substrates has been measured using time domain thermoreflectance before and after a high-vacuum heat treatment at 800 °C for 2 h. While no signs of carbide formation could be detected in as-deposited layers by scanning transmission electron microscopy energy dispersive X-ray spectroscopy elemental analysis, the heat treatment led to partial (W, Mo) or full conversion (Cr, Nb) of the film into carbide. The measured TBC values on as-deposited samples of 315, 220, 220 and 205 MW m^{-2} K^{-1} measured for, respectively, the Cr, Mo, Nb and W samples, were found to not be significantly altered by the heat treatment.

Keywords: Time domain thermoreflectance; Thermal boundary conductance; Metal matrix composites; Refractory metals; Thermal management materials

1. Introduction

Diamond-reinforced metal matrix composites (MMCs) have come into research focus in the past few years as they could potentially be used as highly efficient, thermal expansion-matched heat sinks in microelectronics applications [1]. Indeed, mixing diamond with highly thermally conductive metals such as Cu, Ag or Al allows for composites with a thermal conductivity up to 985 W m^{-1} K^{-1} [2] and a coefficient of thermal expansion (CTE) of between 4 and 8 ppm K^{-1}, covering the CTE range of typical semiconductors in high heat dissipation applications.

One of the key factors that controls the upper limit of the achievable composite conductivity are the diamond–metal interfaces. Indeed, their quality directly influences the diamond–metal thermal boundary conductance (TBC) [5,6], the effect of which significantly increases with decreasing particle size [7].

In Al matrix composites, good results are obtained using Al or Al–Si alloys [3–5] because good adhesion is obtained between the matrix metal and the diamond powder provided the composite processing provides sufficient time at high temperature to form strong interfaces [8]. For pure Cu and Ag, however, the chemical affinity between the metal and carbon is insufficient to form strong interfaces and hence the thermal conductivities of composites using pure metals are rather low, typically significantly below the pure metal's conductivity. This can be overcome by either (i) activating the diamond surface [9], (ii) adding alloying elements with higher affinity to carbon, or (iii) coating the diamond with an adhesion layer. For Cu, adding alloying elements such as B, Cr [6,10] or Zr [11] to the matrix metal yield high composite thermal conductivities, presumably through the formation of a small amount of interfacial carbide [12]. Coating the powder before processing it into a composite has been achieved by sputtering of Mo [13], by the molten salt route [14,15] or by vapor-phase

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deposition of W [16]. The latter process has led to particularly high thermal conductivity of up to 907 W m^{-1} K^{-1} for 100 nm thick coatings, while thicker coatings reduced the beneficial effect. It is, however, unclear whether the conductivity improvement achieved when a carbide is present at the matrix–filler interface is due to an improved interfacial adhesion [17,18], or to the presence of a phase with phononic properties intermediate between those of filler and matrix [19,20], as these effects have both been shown to improve the interface conductance.

A convenient method to measure the TBC at a metal–dielectric interface directly is time-domain thermoreflectance (TDTR) [21,22]. This method uses samples consisting of thin metallic layers directly deposited onto dielectric substrates, and hence has the ability to measure the conductance of a single interface. Using this technique on metal–diamond systems, the diamond surface chemistry was shown to have a strong impact on the TBC between diamond and metals [23–25]. Hydrogen-terminated diamond surfaces were found always to be detrimental to obtaining high TBC [18,24]. This was rationalized by the fact that hydrogen termination also lowers the metal–diamond work of adhesion, thereby weakening the bonds between metal and diamond [18]. By using an oxygen plasma treatment of the diamond surface, it was shown that both a good adhesion and a high TBC can be obtained between a metal and diamond [24,25]. Good adhesion was also shown to be essential to obtain a good TBC even after a heat treatment [26], because such a treatment would otherwise be ineffective or, worse, detach the metallic layer, due to differences in CTE between layer and substrate.

We present here an investigation of the effect on TBC of transforming layers of W, Mo, Nb and Cr deposited on diamond into their respective carbides by high-vacuum heat treatment. The various elements are chosen as the formation of a carbide would provide an interface layer with either lower (Cr), comparable (Mo) or higher (W, Nb) Debye temperature than the metal, the latter being a first-order indicator for the match of the phonon density of states on either side of the interface intervening in phonon elastic scattering theory at interfaces. The TBCs with the diamond substrate are measured by TDTR. The metallic layer composition is determined before and after the heat treatment by transmission electron microscopy (TEM) and the bonding states at the interface are evaluated by X-ray photoelectron spectroscopy (XPS). The results are discussed in the light of the effectiveness of carbide formers in improving the thermal conductivity of diamond-based MMCs and to investigate the predominance of bonding or phonon energy distribution on TBC.

2. Experimental

2.1. Sample preparation

Diamond substrates were purchased from Element 6 (Shannon Airport, Shannon, Co. Clare, Ireland, MWS L25, [100] surface orientation). The [100]-oriented stones were factory-polished, but were further polished using diamond suspensions of 6 μm, followed by 1 μm size. RMS roughness was determined to be less than about 1.5 nm by FIB cross-section. Indeed, no roughness could be distinguished in images resulting from such cross-sections, meaning that if such a roughness exists, it is lower than the detection limit of the instrument. After polishing, the samples were rinsed with acetone, ethanol and isopropanol. The samples were then treated in a Fischione model 1020 plasma cleaner for 15 min. The Ar : O_2 ratio of the plasma was 3:1. Although no time dependence was found after 30 s of plasma treatment [24], the plasma was held for 15 min to remove any layer resulting from surface damage during the mechanical polishing step. This was verified in two ways: (i) the thermal conductivities of all the diamond substrates were verified to be above 1000 W m^{-1} K^{-1}, the value expected for the type of diamond used and the spot size used in the TDTR experiment [24]; (ii) no defects were found in the diamond substrate when performing cross-sectional high-resolution electron microscopy on the samples used for STEM-EDX. The samples were then transferred to a Balzers BAS 450 sputter deposition system and received a layer of Cr, Mo, Nb or W according to the parameters listed in Table 1. The sputtering gas is Ar, at a pressure of 5.2×10^{-3} mbar, and the power of the magnetron depends on the metal, ranging from 500 to 2000 W. Prior to the deposition process, the targets were cleaned for about 5 min in order to make sure that as little surface oxide from the target as possible was included in the resulting layer. Layer deposition rates were calculated by dividing the layer thickness (measured ex situ by cross-section imaging using a Zeiss NVision 500 FIB) by the deposition time.

The TBC between the layers and the substrate was measured by TDTR as described in detail below. The samples were then loaded in an in-house vacuum annealing setup available at the Laboratory of Ceramics, EPFL, in which they were heat treated at 800 °C for 2 h, with a 10 K min^{-1} heat-up speed and a cool-down time of 4 h in a vacuum of 10^{-7} mbar or better.

To study the early stages of the layer deposition, ultrathin (below 2 nm) layers of Mo and Cr were deposited on diamond substrates for XPS investigation. XPS data were collected by an Axis Ultra (Kratos Analytical, Manchester, UK) under ultrahigh-vacuum condition ($<10^{-8}$ mbar), using a monochromatic Al Kα X-ray source (1486.6 eV).

Table 1
Deposition parameters of the metal layers deposited.

Layer metal	Deposition rate [Ås^{-1}]	Thickness [nm]
Cr	6	97 ± 2
Nb	4.5	112 ± 2
Mo	7.9	95 ± 3
W	3.2	106 ± 3
Al	6.0	78 ± 2