Interfacial thermal resistance between the graphene-coated copper and liquid water

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ABSTRACT

The thermal coupling at water–solid interfaces is a key factor in controlling thermal resistance and the performance of nanoscale devices. This is especially important across the recently engineered nano-composite structures composed of a graphene-coated-metal surface. In this paper, a series of molecular dynamics simulations were conducted to investigate Kapitza length at the interface of liquid water and nano-composite surfaces of graphene-coated-Cu(1 1 1). We found that Kapitza length gradually increased and converged to the value measured on pure graphite surface with the increase of the number of graphene layers inserted on the Cu surface. Different than the earlier hypothesis on the "transparency of graphene," the Kapitza length at the interface of mono-layer graphene coated Cu and water was found to be 2.5 times larger than the value of bare Cu surface. This drastic change of thermal resistance with the additional of a single graphene is validated by the surface energy calculations indicating that the mono-layer graphene allows only ∼18% van der Waals energy of underneath Cu to transmit. We introduced an "overall interaction strength" value for the nano-composites based the quantitative contribution of pair interaction potentials of each material with water into the total surface energy in each case. Similar to earlier studies, results revealed that Kapitza length shows exponentially variation as a function of the estimated interaction strength of the nano-composite surfaces. The effect of Cu/graphene coupling on thermal behavior between the nano-composite with water was characterized. The Kapitza length was found to decrease significantly with increased Cu/graphene strength in the case of weak coupling, while this behavior becomes negligible with strong coupling of Cu and graphene.

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1. Introduction

Progress in the area of integrated circuit technologies has led to the rapid growth of semiconductor industry. Currently, silicon and silicon-based materials used in semiconductors have entered the realm of sub-20 nm dimensions in order to meet the demand for low-power, multifunctional electronic chips with high performance and large data storage capabilities [1]. While the reduction in size smaller than 10 nm is a challenge for existing technology [2], the future generation of devices will soon have low-dimensional physics founded by a single or couple of molecular structures. In such cases, graphene has been considered as a key material with potential to overcome the current limitations by providing extraordinary properties such as: high mechanical strength and flexibility [3]; ultrahigh electron mobility [4–5]; and high ther-

mal conductivity [6]. On such direction, one of the main technological accomplishments is the development of various approaches to synthesize graphene on metal substrates [7]. Graphene with a single atom thickness of carbon acts as an ultrathin oxidation-resistant coating with minimal changes in the metal properties [8].

Heat removal is a challenge that restricts the use of graphene-assisted surface coatings in nanoscale devices. The performance and reliability of these devices strongly depends on the efficient dissipation of heat from solid substrates to the surrounding environment or coolant systems. Therefore, understanding the effects of mono- or multi-layers graphene coatings onto thermal transport behavior at the interfaces of graphene-coated-metal structures that neighbor either solid or fluid is critical to thermal management design for new technologies. Recently, the interfacial thermal resistance, known as the Kapitza resistance [9] between liquid and metal/graphene nano-composite has attracted much attention with the objective of obtaining a deeper understanding of heat transport across the interface. For instance, the interfacial thermal

conductance and interfacial phonon transmission coefficients of nano-composite consisting of several layers of graphene sandwiched between silicon crystals were investigated in the study of Shen et al. [10]. Interfacial thermal resistance was found to depend not only on the strictly defined interface properties, but also to associate with the near interface-region when the confined graphene layer is strongly coupled with relatively neighboring materials [11]. Mao et al. [12] used first-principle calculations and an atomistic phonon transport model based on Landauer formalism to demonstrate the strong dependence of thermal transfer on the interlayer separation and stronger bonding of several solid materials with graphene. Chang et al. [13] found a strong dependence of interfacial thermal conductance on the number of graphene layers confined between metal phases. Despite multiple successful studies on metal/graphene systems, there are still very few data pertaining to the thermal behavior of graphene-coated-metal/liquid interfaces. Studies covering liquid water are particularly crucial due to the common use of water in numerous cooling applications for Micro and Nano Electro Mechanical System (MEMS and NEMS).

Over the past decade, molecular dynamics simulations has emerged as a powerful tool to investigate thermal resistance at the interface of solids and water, providing valuable insight into interfacial energy transfer mechanisms. In particular, Kapitza resistance at solid/liquid interfaces are found to depend significantly on the strength of the solid/liquid interaction [14–17], bulk liquid pressure and wettability of solid surfaces [18], the surface temperature [19–22], the interaction energy per unit area of solid/water contact surfaces [23], and hydrophilic headgroups or self-assembly of mono-layers with different chain lengths assigned onto solid surfaces [24]. With extraordinary properties of graphene, the understanding of interfacial thermal resistance at nano-composite surfaces that are composed of mono- or multi-layers of graphene on metal surface and liquid water, is expected to play an important role towards the development of heat transfer and microfluidics devices.

For nano-composites of graphene-coated-metal substrates, water contact angle measurements were employed to characterize the surface energy between liquid water and the nano-composite surfaces [25–27]. The simple Lorentz–Berthelot mixing rule [28] is not a reliable approach to calculate the interaction parameters of non-identical molecules. Hence, the interaction strength between metal/water and graphene/water were parameterized to match the experimentally measured contact angle of the corresponding substrate. This can provide a correct physical behavior for thermal vibrations between solid and liquid, and accurate modeling of the molecular heat transfer mechanisms at the interfaces [29]. The interaction strength between metal substrates and graphene is another important factor that influences the heat transfer across the interfaces of graphene-coated-metal/water systems. For instance, Hopkins et al. [30] found that interfacial chemical bonding of both the phonon flux and the vibrational mismatch has significant influence on the thermal boundary conductance of the metal/graphene. Chen et al. [31] reported that out-of-plane acoustic phonon modes of graphene have significantly changed due to the strong coupled interaction strength between the metal substrate and graphene. In order to simulate the correct behavior of the phase transitions of partially confined copper nanowires inside carbon nanotubes, Guo et al. [32] obtained the Lennard–Jones (LJ) parameter of Cu–C using the mixing rule, and verified that value by first-principle density functional theory (DFT) calculations. Despite the parameter being suitable validated and universally approved in the research of heat transfer performance of metal coated interfaces [13,33], the 14% discrepancy of the binding energies calculated by MD simulations and the DFT approach is not the most suitable for Cu–C interaction strength [32]. Therefore, the dependence of

interfacial thermal resistance on metal/graphene interaction strength needs to be investigated further.

In this work, a series of non-equilibrium molecular dynamics simulations were conducted to investigate the effects of graphene coatings on the interfacial thermal resistance between the graphene-coated-Cu(111) surface and liquid water. We utilized calibrated copper/water and graphene/water interaction strength parameters, which captured the wetting behaviors of the copper and graphite with liquid water. The copper/graphene coupling was also varied to characterize the impact of metal–graphene bonding on interfacial thermal transfer. The Kapitza lengths were measured while the number of graphene layers was varied from 1 to 5 in order to create different surface coating cases. The interfacial energies per unit area of nano-composite having different number of graphene layers with liquid water were theoretically calculated to predict the surface energy of each nano-composite case. We defined an overall interaction strength value between the nano-composite and water based on the quantitative contribution of Cu/water and graphene/water pair interaction potential energies into the calculated surface energy of the nano-composite for each different case. The variation of overall nano-composite/water interaction strength values were employed to characterize the variation of Kapitza length using our earlier exponential dependence theory.

2. Molecular structure and simulation details

A schematic diagram of the simulation structure is shown in Fig. 1. Liquid water was confined between two parallel graphene-coated-Cu(111) surfaces in which the graphene-coated layer faces the fluid. The simulation dimensions were 30.95 Å in the x-direction, 33.28 Å in the y-direction, and the length of the z-direction was adjusted depending on the number of graphene-assist surface coatings. The copper formed by 13 layers of Cu (111) was 25.01 Å thick in the z-direction with an interlayer spacing of 2.084 Å. The number of graphene layers coated on the Cu (111) surfaces was from 1 to 5 and the interlayer spacing between the graphene–graphene and Cu–graphene was 3.4 Å. The liquid density in the middle of the simulation box was set to be close to saturated liquid water density at the corresponding temperature and pressure. Specifically, 2400 water molecules were contained in a volume of 30.95 Å × 33.28 Å × 70 Å, matching the saturated liquid water density of $\rho = 0.9957 \, g/cm^3$ at temperature of 303 K and pressure of 4.5 kPa.

A Cu(111) surface structure was chosen as a solid base in this study as it was the best match with graphene [34] and the growth of graphene on Cu(111) was achieved in an ultrahigh vacuum chamber previously [35]. In particular, the lattice constant of Cu (111) is a_{Cu} = 2.552 Å, while graphene's well-known honeycomb lattice structure matches the triangle-shaped lattice of the Cu (111) surface shown in Fig. 1(b and c). The present lattice constant of graphene is 2.552 Å, which is approximately 3.74% higher than its original value of a_{Gr} = 2.46 Å. The resulting graphene lattice constant has been shown to be a stable atomic structure at the graphene–copper interface, free from any defects or breakage of graphene sheets periodic condition [34,36].

In order to conduct non-equilibrium molecular dynamics simulations of heat transfer through these systems, the outermost layers of both sides of the simulation domains were fixed to their original positions to maintain a system of constant volume. Thermostats were placed at the outermost second and third layers of both solid walls. That means the thermostat reservoirs were small groups of solid atoms next to the outermost layers on the left and right hand side of the system corresponding to hot and cold thermostat regions, respectively. The remains of solid atoms and liquid