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Wetting transparency of graphene deposited on copper in contact with liquid tin

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Abstract

Wetting behavior of liquid Sn (99.99%) on graphene-coated Cu substrate was investigated by the sessile drop method using two testing procedures: 1) classical contact heating (CH) of a couple of materials; 2) capillary purification (CP) allowing non-contact heating accompanied with squeezing the Sn droplet through a hole in an alumina capillary. The tests were performed in vacuum ($p < 1.80 \times 10^{-6}$ mbar) at 360°C for 300 s. The images of Sn/substrate couples were recorded by high-resolution high-speed CCD camera.

The results of this study evidenced that graphene layer is transparent for liquid Sn and after 300 s interaction, it forms the contact angles (θ) similar to those on pure Cu substrates, both in CH ($\theta = 59°$) and CP ($\theta = 32°$) tests. However, with liquid Sn, apparently the same effect of graphene wetting transparency is more complicated than that with water and it is caused by different mechanism, most probably, accompanied with reconstruction of the graphene layer.

Key words: *graphene, liquid tin, sessile drop, wetting transparency, liquophilic, liquophobic*

Introduction

Graphene is “a rapidly rising star on the horizon of materials science” [1] due to its unique structure and exceptional properties for potential high-tech applications. Therefore, pioneering research on the production and characterization of graphene, performed by Andre Geim and Konstantin Novoselov, has been awarded by the Royal Swedish Academy of Sciences for the 2010 Nobel Prize in Physics “for ground breaking experiments regarding the two-dimensional material graphene” [2].

Historically, term graphene was first appeared in 1962 by Hanns-Peter Boehm [3] who described a single-layer carbon foils as a combination of graphite and the suffix-ene.

Graphene represents a crystalline allotrope of carbon in which atoms are densely packed in a regular sp^2-bonded atomic-scale wire of hexagonal honeycomb-like pattern to form one-atom-thick single crystal layer of graphite [1−3]. This unique 2D structure is responsible for extraordinary properties of graphene. Among all other known materials, it is not only the thinnest ever but also the strongest and possesses the highest conductivity of electricity and heat [1−3]. Despite the fact that graphene is the thinnest and almost completely transparent material, however, even helium, the smallest atom from the periodic table, cannot pass through it [1].

As a “mother of all graphitic forms” [1], it is accepted that graphene should possess wetting properties similar to graphite [4] that is known to be hydrophobic [5]. Wettability contact angle (θ) measured between water and graphite surface ranges 90−95° [5] showing that graphite is non-wettable material by water and no penetration of water into porous graphite should take place.

Similarly, several molecular dynamic simulations (e.g. reported in [6,7]) predicted the intrinsic contact angle of water on monolayer graphene between 96° and 102° that is even larger than the contact angle (θ) on bulk graphite substrate. Conversely, recent experimental study by Rafiee *et al.* [8] evidenced that graphene can allow water to pass through and that thin graphene layer does not significantly disrupt the intrinsic wetting behavior of different substrates such as Cu, Au and Si [8]. This phenomenon, called wetting transparency, was also confirmed by molecular dynamic simulations and explained theoretically by Rafiee *et al.* [8] as the effect of extreme thinness of graphene.

However, based on theoretical modelling and exponential confirmation, Shin *et al.* [9] demonstrated that in practice, graphene's wetting transparency is not as perfect as some researchers had suggested. Shih *et al.* [9] showed that wetting transparency of water on graphene breaks down on super-hydrophobic surfaces as well as on super-hydrophylic ones and they described the observed partial transmission of the properties of underlying substrate as wetting translucency instead of wetting transparency. Later research performed by Li *et al.* [4] showed that for both freshly prepared supported graphene and graphite surfaces, the contact angles of water increase after aging in ambient air due to adsorption of hydrocarbons on graphitic surfaces. However, this effect is reversible and it can be partially removed by thermal annealing [4].

It is widely accepted also [8] that scattering in contact angles of pure water on graphene-coated surfaces is related with their roughness since the first studies were performed with the planar substrates on which the deposited graphene formed individual sheets from an interconnected film resulting in increase in the surface roughness by one or two orders of magnitude. Rafiee *et al.* [8] showed that roughness effect in conjunction with the surface chemistry of the graphene sheets may dramatically alter the wettability of graphene-coated substrate by water. On the other hand, the most recent research, performed on graphene-coated copper by Kim *et al.* [10], have evidenced the graphene wetting transparency effect even for roughened copper surfaces although such surfaces are significantly less wettable than graphene itself due to the presence of entrapped air-pockets.

Following the literature data on wetting behavior of water on graphene-coated surfaces, one would expect that depending on testing conditions and substrate surface treatment, different liquids may have dissimilar wetting properties on graphene. However, to best our knowledge, wetting behavior of graphene in contact with high temperature liquids, particularly metallic ones, has not been examined yet. On the other hand, such knowledge is of a great practical importance, particularly for the production of metal-graphene composites and joining dissimilar materials with graphene-coated surfaces using liquid-assisted processes.

This paper reports the results of *in situ* observation of high temperature behavior of liquid tin on graphene layer deposited on Cu foil using two different testing techniques. Tin has been selected as a model metal due to its low melting temperature (229°C) and because liquid tin is well-known to be non-reactive and non-wettable in contact with graphite [11].

Experimental

High temperature wettability tests were performed by a sessile drop method [12] with liquid tin (99.99%) on graphene-coated Cu. The substrate of 15 × 15 mm size was cut from graphene-coated Cu foil prepared using *EasyGraphene™100 mm* System (CVD Equipment Co., USA) according to a proprietary enclosure "Scalable 2D-FILM CVD Synthesis" patent pending [13].

Graphene was deposited on 75 μm thick electrochemically polished Cu foil at 1070°C with 60 sccm H_2 following two-steps process: 1) for 1 h at 160 sccm of 5% CH_4 in Ar and balance of Ar for a total flow of 2 lmp and 2) for 150 s at 320 sccm of 5% CH_4 in Ar with Ar flow adjusted to 2 l. Cooling was done with 1.78 Ar, 60 sccm H_2 and 160 sccm of 5% CH_4/Ar until 650°C. Thereafter, the system was cooled with 2 slm of Ar to 100°C and then offloaded.

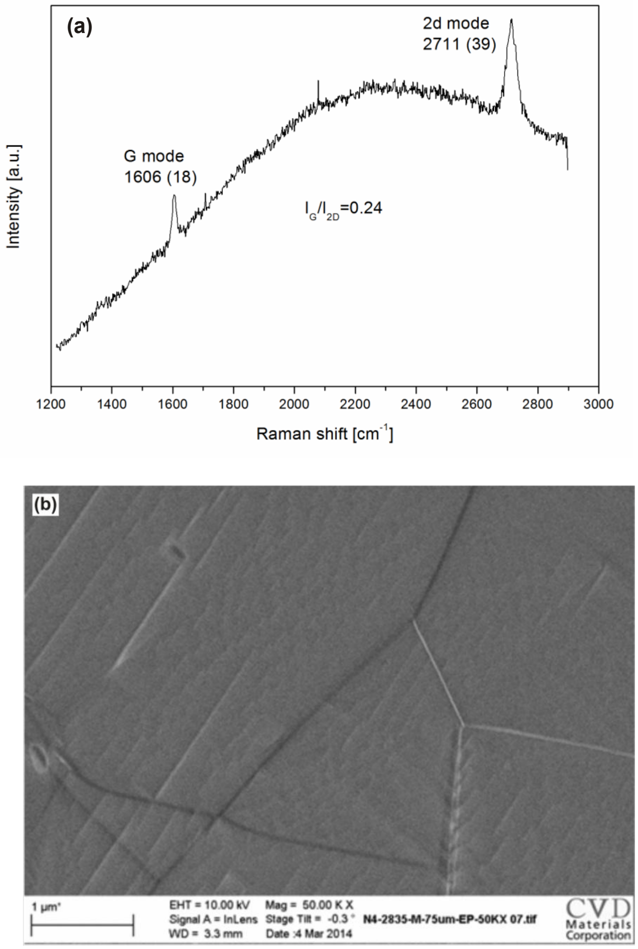

Fig. 1. Surface characterization of graphene layer deposited on Cu foil by (a) Raman spectroscopy and (b) SEM

Raman spectroscopy was used to determine the structure of deposited graphene. Fig. 1a shows that the graphene film displays sharp G (1606 cm^{-1})

and 2D (2711 cm^{-1}) bands with a small ratio of intensity $I_G/I_{2D} = 0.24$, a typical feature of graphene mono layer [14]. Scanning electron microscopy (SEM) image shows the large area uniform growth of the graphene layer (Fig. 1b).

The sessile drop tests were performed under vacuum using experimental complex described in details in [15]. A special testing procedure, called “2in1”, was used allowing to apply simultaneously two testing techniques in one test: 1) classical, commonly used in practice, technique accompanied with contact heating (CH) of a couple of materials from room temperature to experimental temperature and 2) improved technique of separate heating of a substrate and a metal placed in a capillary that was positioned just above the substrate. This technique, known as dispensed drop method or capillary purification (CP), is combined with *in situ* cleaning of a metal drop from native oxide film due to squeezing a drop from a hole in the capillary. CP technique is particularly useful for testing of liquid metals that easy oxidize, such as Sn [15, 16], because the presence of a few nanometer size native oxide film on a metal drop significantly affects both its surface tension [17] and wetting behavior on solid substrates [15, 16, 18].

Directly before loading into vacuum chamber, two samples of tin were cleaned mechanically and ultrasonically in isopropanol (propan-2-ol, $(CH_3)_2CHOH$). Then, graphene-coated Cu (Gn/Cu) foil sample was placed on alumina support located inside tantalum resistant heater of vacuum chamber. One sample of tin for CH test was deposited on graphene-side foil. The second Sn sample for CP test was placed inside an alumina capillary that was positioned above the substrate near the first tin sample, as it is shown schematically in Fig. 2a in comparison with two couples after wettability tests (Fig. 2b).

Following evacuation of gases and getting vacuum of $p = 2 \times 10^{-7}$ mbar by means of a turbomolecular pump, the tantalum furnace was heated to a test temperature of 360 °C with a rate of about 5 °C/min. During heating, gas release was noted at about 140 °C resulting in worsening of vacuum from $p = 2 \times 10^{-7}$ mbar to $p = 6 \times 10^{-7}$ mbar. In the course of further heating, the pressure in vacuum chamber was increased up to one order of magnitude while during 300 s test at a constant temperature of 360 °C, it changed from $p = 1.74 \times 10^{-6}$ mbar to $p = 1.80 \times 10^{-6}$ mbar.

When temperature of 360 °C was reached, the first Sn droplet for CP test was squeezed through a hole in the capillary and also deposited on the substrate near the Sn sample from CH test. Totally six Sn droplets were deposited in the same place to form one CP drop of a volume comparable to that in CH test. After high temperature investigation, the furnace was cooled with a rate of about 10 °C/min. During heating and cooling, the images of CH and CP couples were recorded by means of high-speed high-resolution camera MC1310 with a rate of 10 frames per second (fps) for whole course of the test, except the moment of squeezing the Sn drop through the capillary that was recorded with a rate of 50 fps. The collected images were used for estimation the contact angle values (either manually or by calculation with a use of ASTRA2 software) [19, 20] as well as for making a real-time movie of high temperature experiment (see *Supplementary information*).

For reference, the sessile drop tests were also performed under the same testing conditions with pure Sn (99.99%) on polished graphite substrates using both improved CP procedure and classical contact heating (CH) technique [15, 16].

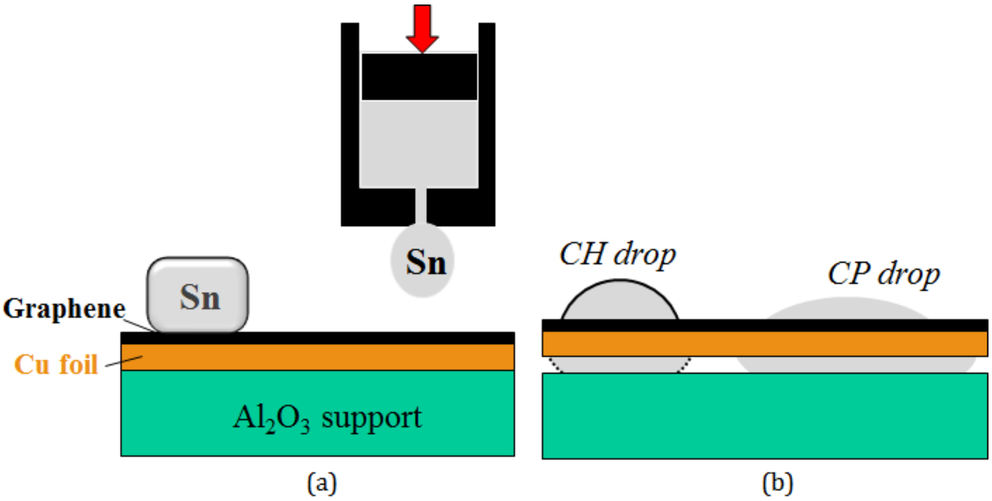

Fig. 2. Schematic presentation of the sessile drop wettability test of Sn on Cu foil covered with graphene layer using improved testing procedure “2in1” allowing application of simultaneously two techniques (CH – contact heating; CP – capillary purification): (a) before test; (b) after test

Results and discussion

The selected images of CH and CP couples for the most representative stages of wettability tests are shown in Fig. 3 and Fig. 4, respectively. Comparison of wettability kinetics for two testing techniques is given in Fig. 5. The measurements of contact angle values of recent wettability tests are collected in Table 1 and Table 2 and compared to those from the previous study of wetting properties of Sn/Cu couples performed using the same testing procedure and equipment [16].

Visual observation of the behavior of Sn sample in CH test (Fig. 3, *Supplementary information*), suggests that the sample remained solid after reaching melting temperature of tin (T_m = 229°C) while the beginning of Sn melting was notable at about 250°C. This contradiction is apparent because of the presence of primary oxide film covering the surface of the Sn sample in CH test. Moreover, this oxide film is continuous and quite strong thus affecting the shape of the molten sample that is not drop-like and becomes spherical and symmetrical after prolonged time of heating under vacuum. Similar behaviour of the Sn samples, affecting contact angle measurements, was observed in CH tests of this study on graphite substrates as well as of previous research [16] on Cu (99.99%) substrates under various time-temperature-atmosphere conditions. Comparison of the experimental data collected in Table 1 suggests that the effect of primary oxide film on the contact angle values becomes less pronounced with increasing temperature and getting better vacuum (by decreasing of pressure in a vacuum chamber).

At the beginning of CH test (t = 0 at 250°C) on graphene-coated Cu substrate (Gn/Cu), the Sn drop formed a contact angle of θ_0 = 64° that successfully decreased to θ_{300} = 59° after 300 s interaction. Under similar time-pressure conditions in CH tests, this value is comparable to that on pure Cu substrate at 230°C (θ = 50°). But it is much lower than the values one would expect on graphene taking into account very high contact angles measured in CH tests on graphite substrates under varying testing conditions (θ = 125−142°, Table 1). During further temperature ramping up to 375°C (510 seconds from the beginning of CH test), the contact angle falls up to θ_{510} = 47°. It is need to be pointed out, that during further cooling from 375°C, the contact angle of Sn/Gn/Cu system continues to decrease up to θ_{1170} = 39° at T = 250°C and θ_{1320} = 37° at 230°C, respectively.

In contrast to CH drop, the Sn droplets squeezed from a capillary in CP test were exempted by primary oxide and showed perfect shape. Therefore, wetting behaviour of all CP droplets placed on the same substrate was similar showing high repeatability of kinetics related to contact angle *vs.* time (*Supplementary information*).

Shortly as the first squeezed Sn droplet was deposited on graphene-coated copper, it formed the contact angle of θ_0 = 41° and spread very quickly over graphene layer. The same behavior was recorded for each successively deposited droplet up to six droppings to form one CP drop of a volume comparable to that of Sn drop in CH test. This last CP drop formed θ_{300} = 32° and exhibited the same effect of wetting improvement during cooling as CH drop, starting from θ_{510} = 25° at 370°C to θ_{1170} = θ_{1320} = 21°, respectively (Table 1). However, these values are almost two orders of magnitude lower compared to those in CH test (Fig. 4).

It should be highlighted that despite the presence of an oxide film on the Sn sample in CH test its interaction with the substrate took place during heating from T_m to 360°C. This process was accompanied with movement and raising the substrate to the top with its slight tilting in the place where CP drop was later deposited and hold at 360°C. As a consequence, it was difficult to perform calculations of the CP contact angles with ASTRA2 software and hence the results were measured manually. Moreover, wetting of Gn/Cu substrate accompanied with its movement inside Sn droplets, both CH and CP ones, allowed the measurements of contact angles formed with Sn(Cu) drops (i.e. Sn drops already containing dissolved Cu due to their high temperature interaction with Cu substrate) on the Al_2O_3 support, as it is schematically presented in Fig. 2b.

CH and CP drops do not wet alumina showing slightly higher contact angle values of 168° for CH and 162° for CP test, respectively. Despite possible deformation of the drop shape due to the presence of Gn/Cu layer inside the Sn drops, these values are in agreement with those recently reported for liquid Sn (99.99%) on alumina in the work [21] (Table 1).

The results obtained in this study showed clear evidence of the effect of primary oxide film on the Sn sample on wettability kinetics that is particularly well distinguished in Fig. 4. The relationship in CP test between θ *vs.* time is almost liner while the θ = f(t) curve is smooth. Non-perfect shape of the Sn drop in CH test caused unusual changes in the contact angle values for the period of the test starting from 64° at t = 0, decrease to 56° after 120 seconds and increased to 59° after 300 seconds. Nevertheless, the presence of primary oxide film does not affect the transparency of the graphene layer for liquid Sn and its wetting behavior is comparable to that on pure copper substrate but not on graphite.

Visual observations of the solidified sessile drop couples presented in Fig. 2b and Fig. 6 indicate that liquid Sn passed through graphene layer, wetted Cu substrate and formed one large drop Sn(Cu) with graphene-coated substrate within. The detailed structural characterization of Sn/Gn/Cu couples produced in CH and CP tests, particularly that of Sn(Cu)/Gn interfaces, is under progress and will be reported in the next communication.

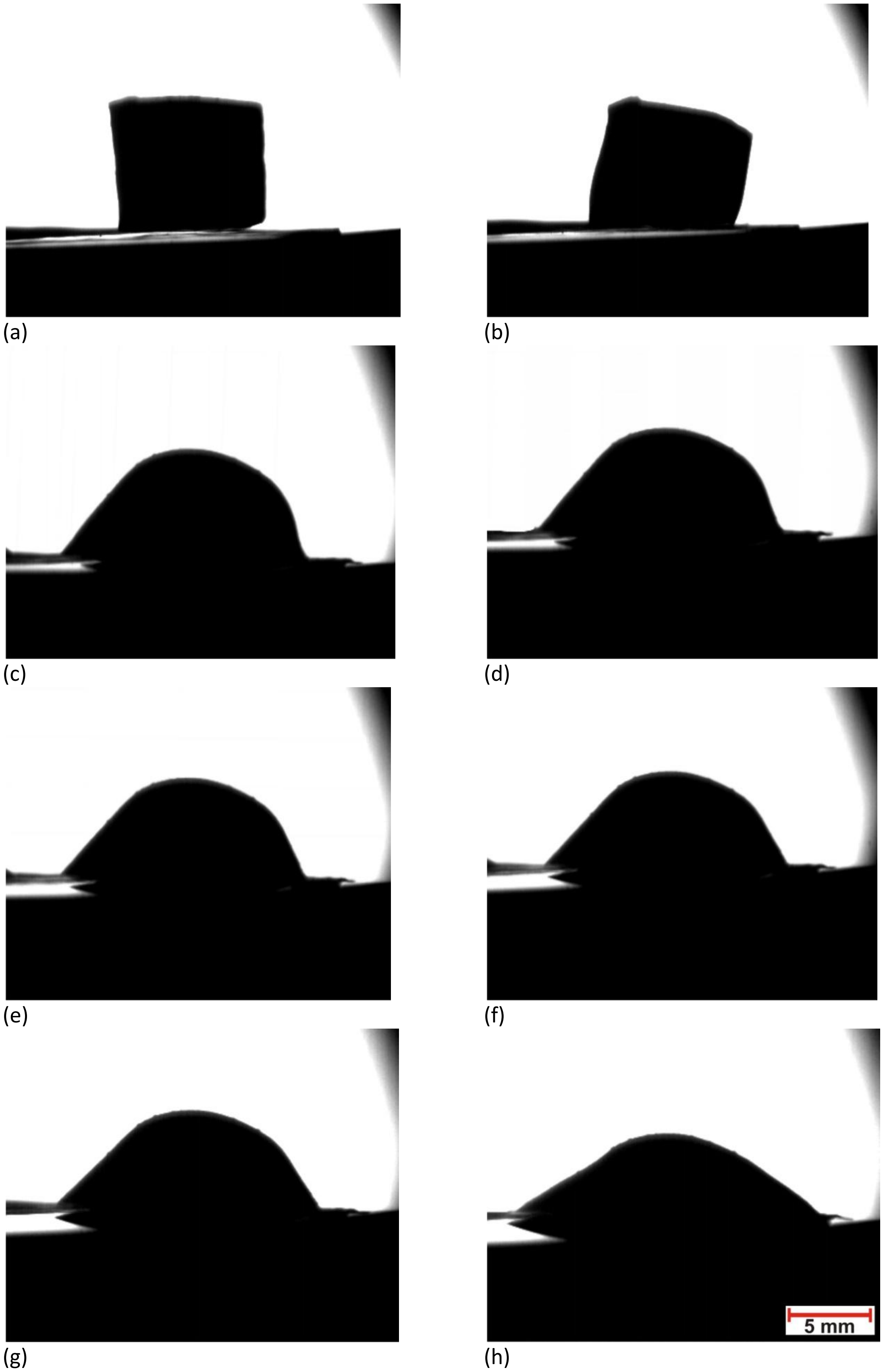

Fig. 3. Images taken from CH test of Sn/Gn/Cu couple (360°C; 300 s): a) couple before test; b) the beginning of melting (at about 250°C); c) the beginning of test – t = 0 s; d) t = 75 s; e) t = 150 s; f) t = 225 s; g) the end of the test – t = 300 s; h) after solidification

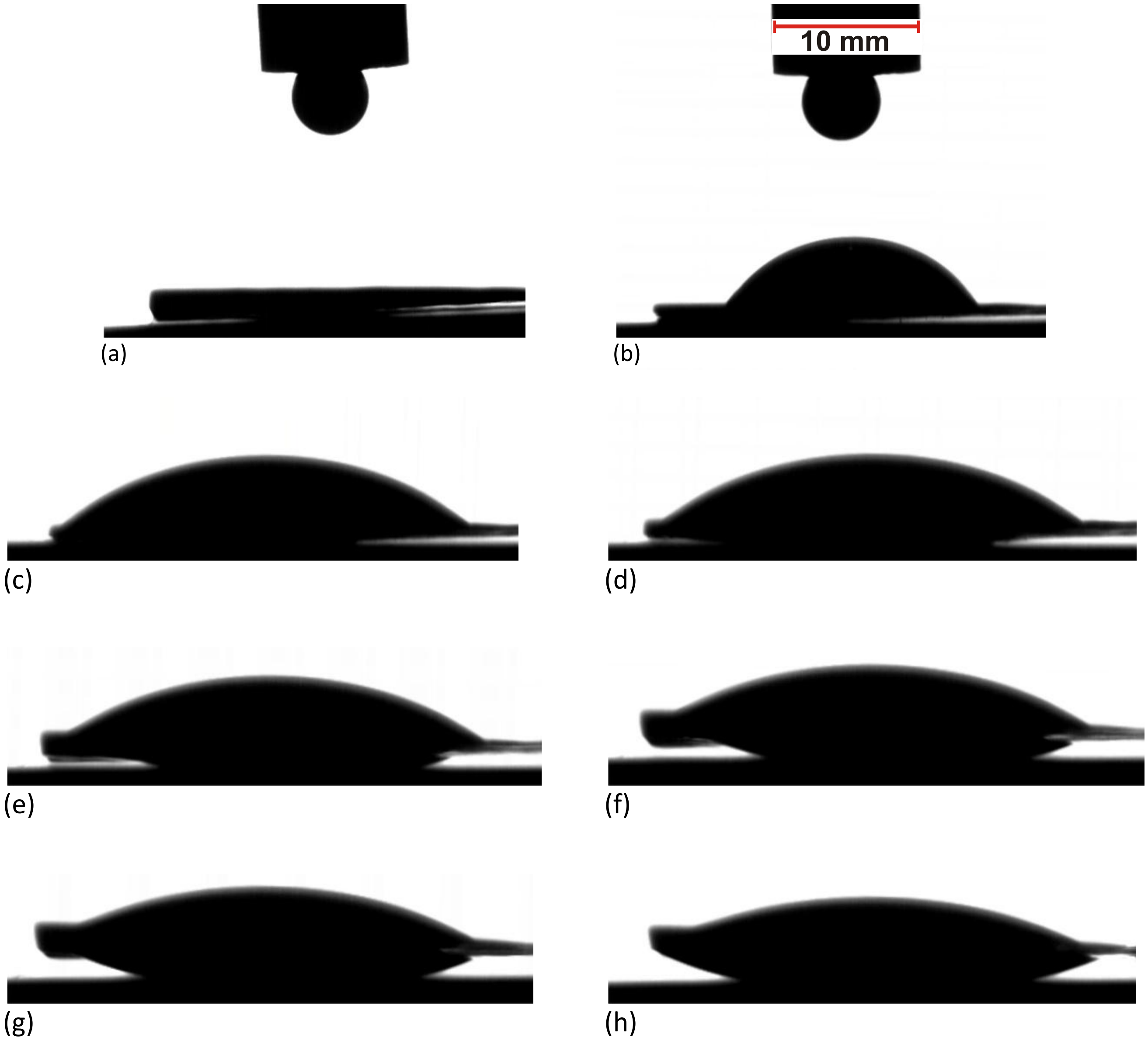

Fig. 4. Images taken from CP test of Sn/Gn/Cu couple (360°C; 300 s): a) the start of metal dropping from a capillary – 1st drop; b) the end of dropping from a capillary – 6th drop (last drop); c) the beginning of test – t = 0 s; d) t = 75 s; e) t = 150 s; f) t = 225 s; g) the end of the test – t = 300 s; h) after solidification

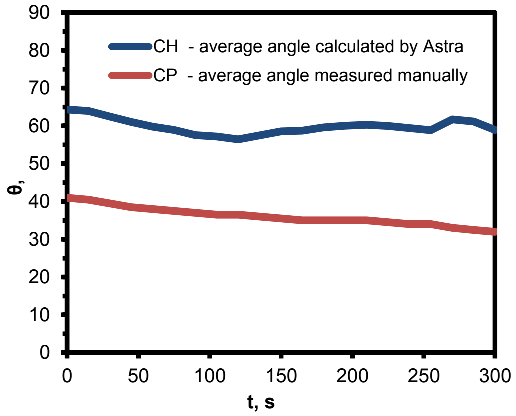

Fig. 5. Wettability kinetics of liquid tin (Sn 99.99%) on graphene-coated Cu foil recorded at 360°C for 300 s using two testing techniques: CH – contact heating; CP – capillary purification

Table 1. Comparison of contact angle values measured by the sessile drop method using contact heating (CH) and capillary purification (CP) techniques with liquid Sn (99.99%) on pure Cu (99.99%), graphite (C_{gr}) and alumina

Substrate	**Testing conditions**				**θ, °**	**Ref.**
	Procedure	**Atmosphere**	**T_{exp}, °C**	**Time, s**		
Cu	CH	air	230	300	136	[16]
	CH	vac. 4 × 10^{-6} hPa	230	300	99	
	CH	vac. 3 × 10^{-6} hPa	230	300	60	
	CH	vac. 2 × 10^{-6} hPa	230	300	52	
	CH	air + flux	230	300	47	
	CP	vac. 3 × 10^{-6} hPa	230	300	23	
C_{gr}	CH	vac. 2 × 10^{-5} hPa	260	600	130	This work
	CH	vac. 5 × 10^{-6} hPa	360	600	125	
	CH	vac. 2.3 × 10^{-6} hPa	250	900	142	
	CP	vac. 7.4 × 10^{-7} hPa	250	300	128	
Al_2O_3	CH	vac.	250		173	[21]
			860		158	

Table 2. Comparison of contact angle values measured by the sessile drop method using contact heating (CH) and capillary purification (CP) techniques for liquid Sn (99.99%) on graphene-coated Cu foil and at Sn(Cu)/Al_2O_3 interface with Sn(Cu) drops produced by "2in1" procedure at the Al_2O_3 support

Substrate	**Testing conditions**				**θ, °**		
	Procedure	**Atmosphere**	**T, °C**	**Time, s**	**Designation**	**CH**	**CP**
Gn/Cu	2in1	vac. 1.8 × 10^{-6} hPa	360	0	θ_0	64	41
			360	300	θ_{300}	59	32
			375	510	θ_{510}	47	25
			250	1170	θ_{1170}	39	21
			230	1320	θ_{1320}	37	21
Al_2O_3*	2in1 for Sn/Gn/Cu couple on Al_2O_3		360	300	θ_{300}	168*	162*

θ_0 – contact angle at the beginning of the test (t = 0) at 360 °C; θ_5 – contact angle after 300 seconds at 360 °C; θ_{510} – contact angle after 510 seconds from t = 0 and corresponding T = 375 °C; θ_{1170} and θ_{1320} – contact angles formed during cooling after 1170 seconds (250 °C) and 1320 seconds (230 °C) from t = 0, respectively; CH – calculated using ASTRA2 software; CP – manually measured; * – manually measured contact angles formed between Al_2O_3 support and the Sn(Cu) drop

Based on the experimental results obtained in this work, it can be concluded that liquid Sn does not "see" thin graphene layer and its wetting behavior is similar to that on pure Cu substrate. Following the terminology used for wetting phenomena of water, the graphene-coated copper may be defined as *hydrophilic*. However, taking into account different nature of molten metals, compared to liquid water, as well as the role of high temperature in their interaction with solid substrates, J.J. Sobczak [22] proposed to use another terms, i.e. *liquophilic* and *liquophobic* corresponding to well-wettable and non-wettable surfaces in contact with different liquids, including metals.

In English, the terms *hydrophilic* and *hydrophobic* came from the Greek language and they both refer to water ("hydro") while "philo" and "phobos" always mean that there is a positive and negative meaning for something, respectively [23]. Thus, following the Greek word philosophy, the most suitable and universal terms casing all liquids are *liquid-(o)-philic* and *liquid-(o)-phobic*, correspondingly [23], those are in agreement with terminology proposed by J.J. Sobczak [22].

It should be highlighted that interaction between liquid tin and graphene-coated copper and thus corresponding mechanism of graphene wetting transparency are different from those in the water/graphene couples because of dissimilarities of both testing conditions (UHV, high temperature) and the nature of liquid. Moreover, the formation of Sn drop at the bottom-side of Cu foil suggests that under testing conditions used in this study, liquid Sn passes through the graphene

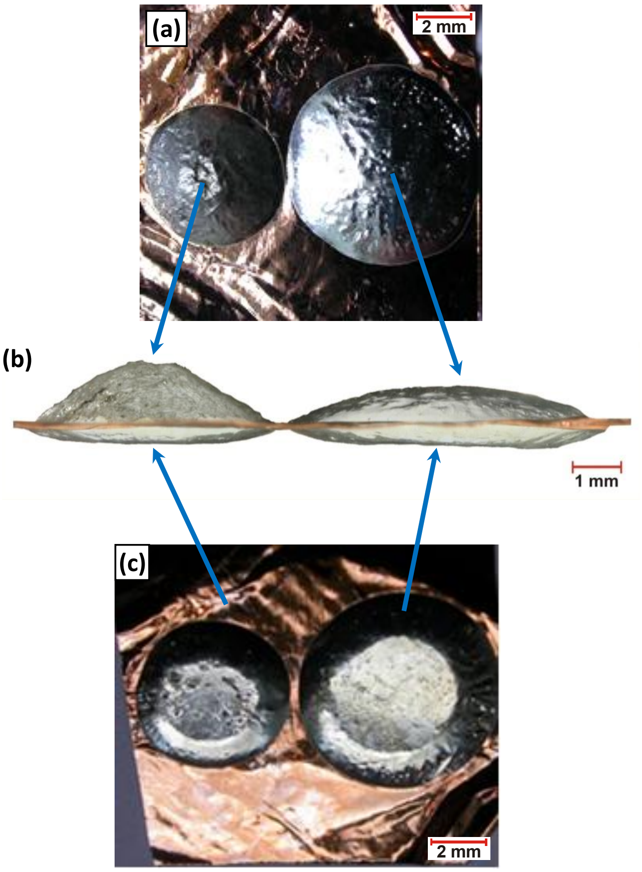

Fig. 6. Photos of solidified sessile drop sample showing top view on graphene coated Cu foil (a), side view (b) and bottom view from graphene-free Cu surface (c) of two Sn droplets deposited on graphene-coated Cu foil by CH (left droplet) and CP (right droplet) technique

layer. Such a mass transfer might be an experimental evidence for existing of some discontinuities in initially continuous graphene layer.

As reported by Zan *et al.* [24,25] and Ramasse *et al.* [26], in the presence of metals graphene can be etched on the nano-scale under exposure to UHV. However, later research by Zan *et al.* [27] evidenced spontaneous self-healing of nano-holes in graphene layer. This reconstruction by hole-filling and re-knitting processes is accompanied with either knocking of carbon atoms out from neighboring edges or supplying by nearby hydrocarbon contamination patches. Therefore, it cannot be excluded that similar holes in graphene layer may form and even grow under conditions of this study, i.e. either due to heating in UHV and/or due to interaction of graphene layer with liquid Sn. These holes may present the openings for the direct interaction between Sn and Cu atoms accompanied with mass transfer through the freshly formed Sn/Cu interface. Furthermore, it was showed experimentally that the Sn/Cu couple is extremely reactive and even subsecond interaction of liquid Sn with Cu is sufficient to form intermetallic compound at the interface [28]. These findings suggest that wetting transparency of graphene observed in this study is dominated by the presence of discontinuities in the graphene layer and more work is needed to proof whether the reconstruction of graphene layer can take place at high temperature under UHV in the presence of liquid tin and how it is affected by kinetic factors and possible mechanisms of graphene reconstruction at different stages of Sn-graphene and Sn-Cu interactions.

Summary

Comparison of the results of this study with previous observations of Sn/Cu couples [16] suggests that graphene does not play the role of a barrier layer for Sn atoms and graphene-coated copper is *liquophilic* in contact with liquid Sn. However, with liquid Sn, apparently the same effect of graphene wetting transparency is more complicated than that with water and it is caused by different mechanism, most probably, accompanied with reconstruction of the graphene layer.

The observations presented in this work could have important implications in design and process development of graphene-metal composites or joining dissimilar graphene-coated materials by liquid-assisted methods.

Acknowledgment

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Supplementary information

https://tv.iod.krakow.pl/89/wetting-transparency-of-graphene-deposited-on-copper-in-contact-with-liquid-tin/

The movie represents the real-time high temperature behavior of liquid tin on graphene-coated Cu foil during heating to testing temperature as well as during cooling down to room temperature.

The left color bar represents the temperature changes upon the test.