



Effect of graphene coatings on the morphology of submillimeter thin copper wires after salt spray aging

Krzysztof Lis, Krzysztof Placek, Spyros Diplas, Martin F. Sunding, Sandeep M. Gorantla, Grażyna Gryglewicz, Alicja Bachmatiuk

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Abstract Unprotected copper conductors are prone to oxidation and corrosion, especially when in contact with salt water or at high temperature. In this study, we compared commercially available coating with graphene oxide and plasma-enhanced chemical vapor deposition (PECVD) graphene coated wires in terms of antioxidation and anticorrosion protection. Samples were subjected to aging tests in a salt spray chamber. Thereafter, both the degree of coverage and surface protection were assessed by X-ray photoelectron spectroscopy measurements and scanning electron microscope images, which showed significant surface protection for both graphene coatings. Raman spectra obtained from the transferred coatings revealed their

structural stability, which shows that it is possible to successfully use few atomic-layers-thick coatings to protect commercially available wires. Wire resistance tests performed at temperatures up to 320°C showed similar or better results for graphene coatings than for commercially coated wires. Additionally, images of the wires after high temperature tests showed high antioxidation protection for graphene coatings, especially for PECVD. The results of this study can be applied for further research on mechanical suitability of the coatings and wires themselves, especially after high-temperature CVD processes. Such studies may lead to novel Cu wire processing technologies.

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K. Lis (✉), K. Placek, S. M. Gorantla, A. Bachmatiuk (✉)
Łukasiewicz Research Network – PORT Polish Center for
Technology Development, Stabłowicka 147, 50-066
Wrocław, Poland
e-mail: krzysztof.lis@port.lukasiewicz.gov.pl

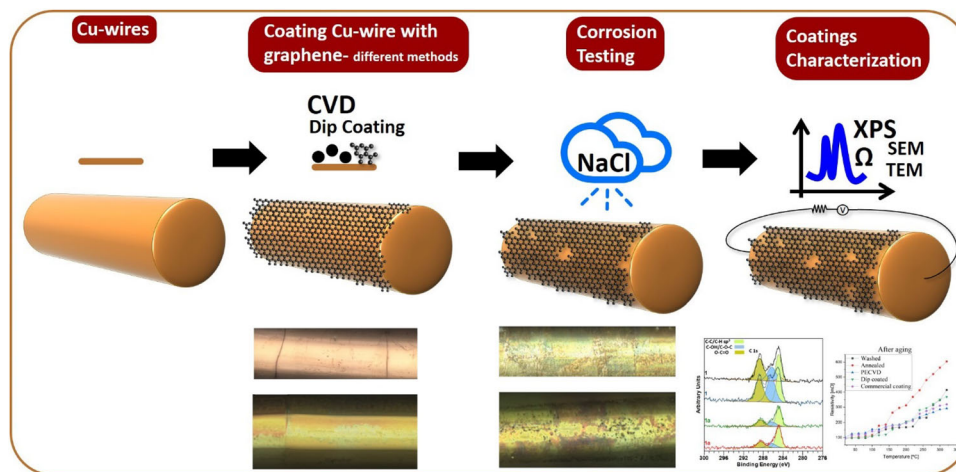
A. Bachmatiuk
e-mail: alicja.bachmatiuk@port.lukasiewicz.gov.pl

K. Lis, G. Gryglewicz
Department of Process Engineering and Technology of
Polymer and Carbon Materials, Faculty of Chemistry,
Wrocław University of Science and Technology, Gdańska 7/
9, 50-344 Wrocław, Poland

K. Placek
Institute of Low Temperature and Structure Research, PAS,
2 Okolna St., 50-422 Wrocław, Poland

S. Diplas, M. F. Sunding
Department of Sustainable Energy Technology, SINTEF
Industry, Oslo, Norway

Graphical abstract



Keywords Graphene coating, Copper wires, Aging and corrosion

Introduction

Unprotected copper (Cu) conductors are prone to oxidation and corrosion, especially when used in relatively high-power electrical devices.^{1–3} Traditional covers, such as plastic or varnish coatings, can be thick and breakable, leading to local damage and corrosion. Therefore, it is crucial to obtain new and more effective methods of protecting the copper surface in wires. One of the main candidates for protective coating is graphene.^{2,4–7} It offers many advantages as a coating cover; even a layer with a thickness of one atom can protect the surface against both oxidation and corrosion associated with moisture and aggressive ions, such as chlorine. Additionally, graphene is characterized by high flexibility, high adhesion to the surface, and high mechanical strength, which allows for complete coverage of irregularly shaped surfaces.^{8,9}

In recent years, these properties are associated with research related to its application both as coating developed on the copper surface by direct synthesis^{2,9–13} and graphene oxide coating developed on conductors from the solution.¹⁴ However, the studies focused on a specific processing method of applying graphene to wires, e.g., chemical vapor deposition (CVD) or coating with graphene oxide from a suspension in a solvent, followed by the structural evaluation of the obtained coatings. Therefore, the results obtained in these studies are difficult to compare with each other owing to the discrepancies, both in the properties of the conductors themselves (i.e., diameter, copper purity, etc.) and types of tests conducted for the purpose of evaluation.

In this study, we investigated the antioxidation and anticorrosion performances of as-grown and dip-coated graphene together with commercially available varnish coatings. All of these coatings have their advantages and limitations; however, they have not been tested under the same conditions to assess their suitability in common applications. For graphene coatings to be introduced into production, they must be competitive to the coatings currently used, and their production must be relatively simple and inexpensive. This applies to both the coating process itself and the quality requirements of the coated material.

Direct synthesis of graphene on the copper surface is accomplished by CVD, which allows the complete coverage of copper with a controlled number of layers.^{2,10} Theoretically, this is the most promising coating method; however, it is difficult to achieve in practice. Conducting synthesis includes the need to control the composition of the reaction atmosphere, pressure, and temperature, as well as to maintain constant parameters of the substrate.

For the CVD processes, the primary problem is the high temperature during synthesis, approximately 1000°C. Although the process itself does not oxidize the wire surface, it changes its crystal structure, and often deteriorates its mechanical properties. Plasma-enhanced chemical vapor deposition (PECVD) was chosen as the target process to shorten the reaction time and reduce the heating time.

Materials and methods

Commercially available copper wire (99.9% pure) of 0.1-mm diameter was divided into 10 cm long samples. Thereafter, the samples were placed in a solution of acetone:isopropanol:ethanol = 1:1:1 and subjected to

Table 1: Summary of samples discussed in the study

Sample name	Code	Description
Washed	1/1a	Washed wire
Annealed	2/2a	Washed, annealed 1000°C, 15 min
PECVD	3/3a	Washed, annealed, synthesis 1000°C, 1 min
Dip coated	4/4a	Dip coated (5 × 20 mm/min)
Commercial coating	5/5a	Coated with commercial varnish

^a- after aging in salt spray chamber for 48 h

an ultrasonic bath for 15 min; subsequently, they were rinsed with de-ionized water. To remove the oxides layer, samples were immersed in acetic acid for 30 s, followed by rinsing and drying. Thus, washed samples were prepared.

Annealing and graphene growth were conducted in a low-pressure PECVD system with a 13.56 MHz RF plasma generator. Cu wire samples were placed in the center of a 30-cm heating zone of a quartz tube 65 mm in diameter. Annealing was performed for 15 min at a pressure of 20 Pa and an H₂ flow of 10 sccm. Following the annealing procedure, the synthesis was commenced by adding 20 sccm of methane and turning on the plasma generator at 200 W. The synthesis was conducted for 1 min.

For the preparation of dip coated samples, graphene oxide (GO) obtained by the modified Hummers' method was used.¹¹ Cu wires were immersed five times at the rate of 20 mm/min in ethanol containing 10 mg/cm³ of GO.

A wire with a commercial polyurethane varnish, with a coating thickness between 4.5 and 5.5 μm, was selected as the available commercial reference point.

Aging process was conducted in a WEISS SC/KWT 450/SO salt spray chamber for 48 h. The salt spray test was conducted using salt solution of 3 wt% NaCl with a spray volume of 600 cm³/h at a constant temperature of 50°C.

Surface material transfer for further characterization was accomplished with the aid of poly(methyl methacrylate) PMMA and copper etching. Samples were dipped in PMMA solution and spun on a spin coater to obtain uniform coverage. Thereafter, the PMMA coating on one side of the wires was mechanically removed, allowing them to be placed in a 1 M solution of ammonium persulfate for etching. Subsequently, the samples were transferred to deionized water several times, to remove contaminants, and then to wafers or TEM grids. The PMMA coating was removed with acetone vapors yielding imaging-ready samples.

XPS measurements were obtained with Axis Ultra spectrometer with mono Al K α X-ray source (1486.6 eV). Pass energy for survey spectra was

80 eV, and for detail spectra it was 40 eV. Peaks were fitted based on studies related to the analysis of the spectrum of copper and graphene oxide.^{12,13}

SEM imaging was performed in a FEI Helios NanoLab 450 scanning electron microscope. An accelerating voltage of 2 kV and a TLD detector were used for imaging.

High resolution transmission electron microscopy (HRTEM) images of graphene and GO after transfer were obtained with FEI Titan G2 60–300 double corrected scanning transmission electron microscopy (STEM) at 80 kV.

Resistance measurements were performed using a Keithley 2700/E precision multimeter at a current of 0.1 A on 2-cm wire sections. Measurements at room temperature were obtained by soldering the wire to the contacts. For elevated temperature measurements, the wire was placed on a glass substrate and attached to contacts with silver paste. Thereafter, it was heated on a hot plate. The resistance measurement was performed during the heating of the sample, measuring every 20°C in the range from 20 to 320°C. Each measurement was repeated five times, considering the mean of the obtained values as the result.

Results and discussion

In this work, we compared commercial and graphene coatings in terms of their effectiveness in protecting copper wires against oxidation and corrosion. Five types of samples were prepared, including three coated and two unprotected, see Table 1 for reference.

Coverage and corrosion protection

To evaluate the effect of the obtained coatings, the samples were subjected to aging tests in a salt spray chamber, and both the degree of coverage and surface protection were assessed.

Figure 1 shows optical microscope images of clean, annealed, CVD graphene covered, dip coated, and

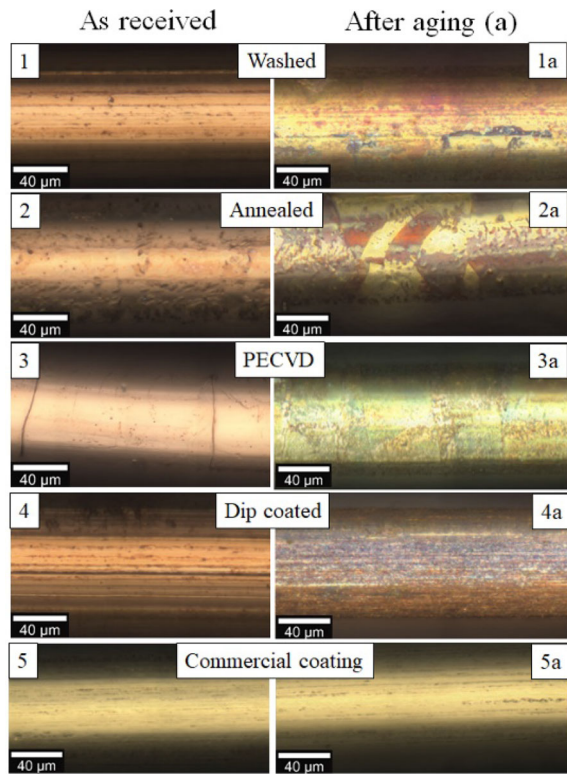


Fig. 1: Optical microscope images of Cu wires before (left) and after aging (right): (1, 1a) washed, (2, 2a) annealed, (3, 3a) with CVD graphene, (4, 4a) GO coated and (5, 5a) commercial varnish coating

commercially coated Cu wires before (1–5) and after aging (1a–5a). Pre-aging images show the effect of heat treatment (2, 3) on changes in the surface morphology. A smooth surface and presence of deformations can be observed for both the annealed sample and PECVD owing to the high temperature and low pressure of the process. After aging, washed (1a) and annealed (2a) wires form brown color due to the formation of Cu_2O and $\text{Cu}(\text{OH})_2$, which are identified on XPS spectra (Fig. 2). The obtained images show some heterogeneity in the coating, with different colors in some places, but overall the changes are uniformly spread on the entire surface of the coated wires (Fig. 3a–5a), which suggests good coverage. Samples after PECVD and commercial varnish show clear surface protection, whereas dip coated samples show some surface protection with dark areas.

To determine the effects of aging on the surface of tested wires, XPS measurements were performed. Bare copper oxidizes even at room temperature in contact with air, which is further accelerated in the aging chamber in the presence of salt spray.^{1,14} Various oxides can form on the wire surface,^{14–16} thus two main reactions can be distinguished for cuprous oxide and copper hydroxide formation:

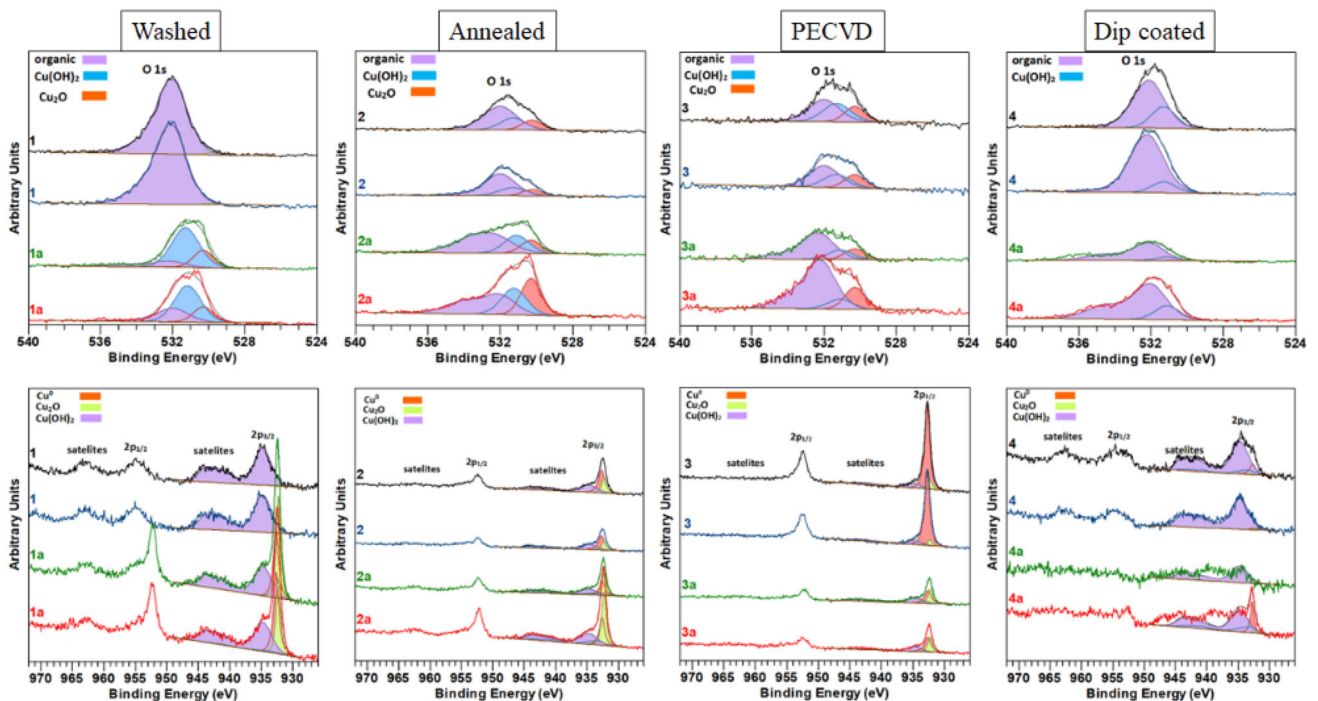
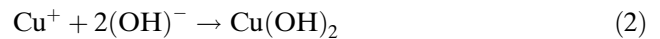


Fig. 2: XPS spectra of O1s (top) and Cu2p (bottom) peaks acquired from Cu wires

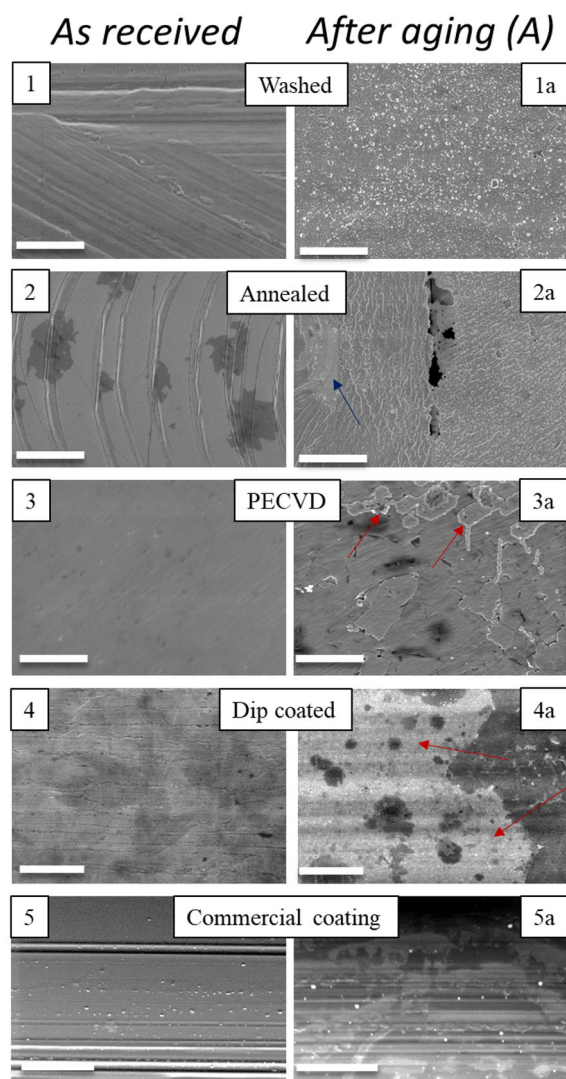


Fig. 3: SEM images of Cu wires before (left) and after aging (right): (1, 1a) washed, (2, 2a) annealed, (3, 3a) with CVD graphene, (4, 4a) GO coated. Scale bars: 1 μm

Therefore, observing significant increase of Cu_2O or $\text{Cu}(\text{OH})_2$ in XPS spectra obtained from all aged samples (1a–4a), it can be assumed that the copper surfaces are not well protected from environmental influence. The obtained results in the form of O 1s (top) and Cu 2p (bottom) peaks are presented in Fig. 2. The wires that were washed and coated with graphene oxide before aging show peaks associated with $\text{Cu}(\text{OH})_2$ on the surface. The annealed wire surface shows a mix of metallic Cu, Cu_2O , and $\text{Cu}(\text{OH})_2$; on the PECVD wire, metallic Cu is dominant at the surface. After aging, PECVD (3a) wire shows presence of Cu_2O with some metallic Cu at the surface, and samples 1a, 2a show a mix of Cu_2O , and

$\text{Cu}(\text{OH})_2$. In addition, sample 4a mainly shows presence of $\text{Cu}(\text{OH})_2$. After aging, a significantly higher Cu_2O presence can be observed for samples 1 and 2 as compared with samples 3 and 4. Therefore, some protection against corrosion occurs in samples with graphene and GO coatings.

Scanning electron microscopy images (Fig. 3) show both the degree of surface coverage in graphene and graphene oxide, as well as the effect of the salt spray test. On the annealed (2) wire, graphene domains with one to few atomic layers and a size up to 2 μm are visible. The residual carbon material from the wire production process causes a micro scale growth of graphene on the copper surface. PECVD and dip coated wires (3, 4) are fully covered, with darker areas being visible in both cases, thus providing evidence of more layers of carbon material. Commercially coated wire is uniformly coated. After aging, the surfaces of samples 1a and 2a are completely covered in copper oxide, except for small fragments of graphene shielded for sample 2a (blue arrow). In the case of sample 3a, only partial coverage of the surface by Cu_2O (red arrows) is visible. Similarly, in sample 4a, the surface shows both an intact graphene oxide coating and fragments completely covered with Cu_2O . Sample 5a shows significantly brighter areas possibly related to salt spray penetration through the varnish and subsequent partial oxidation.

Using the components of the C1s XPS spectra allows us to observe the influence of the aging process on the chemistry of the carbon material on the copper surface. Washed wire shows carbonate species (1) notably reduced after aging (1a), with the strongest signal for C–C/C–H junctions in sp^3 hybridization. Dip coated wire shows similar XPS spectra; however, the π – π^* satellite peaks indicate the presence of sp^2 bond carbon. The annealed wire shows typical spectra for organic surface contamination, with an increased presence of C–OH/C–O–C bonds after aging. The samples after the PECVD process, show dominant signals from carbon–carbon bonds with an increased presence of C–OH/C–O–C bonds after aging. These results indicate a partial degradation of the graphene coatings as a result of the aging process (Fig. 4).

Coating quality assessment

The assessment of the impact of graphene coatings on the surface of the wires was supplemented with an analysis of the durability of the coatings themselves.

Due to the high fluorescence signal when imaging graphene directly on copper, it was decided to perform a transfer onto a silicon wafer in order to measure the coatings parameters.¹⁷ The Raman spectra of the material transferred to wafers show presence of carbon peaks for samples 2, 3, and 4, both before and after

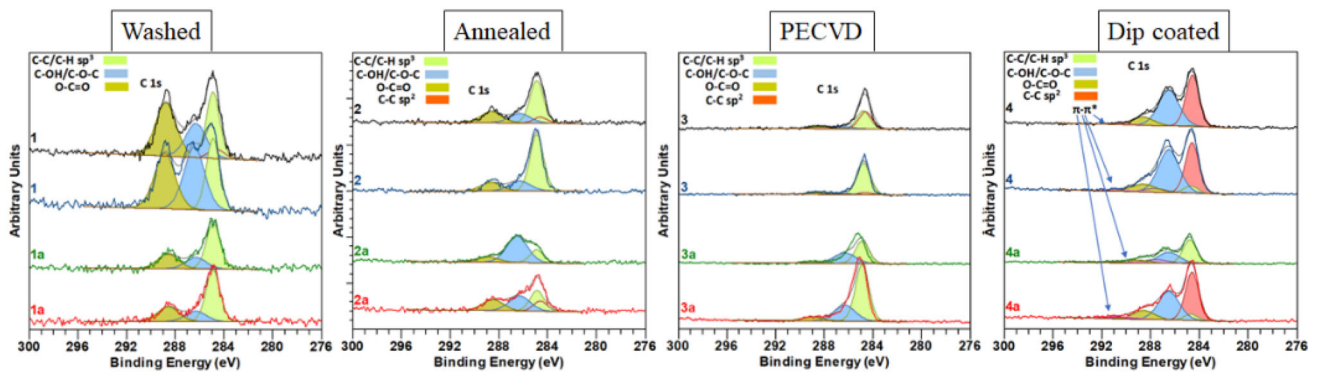


Fig. 4: C1s peaks from XPS spectra acquired from Cu wires

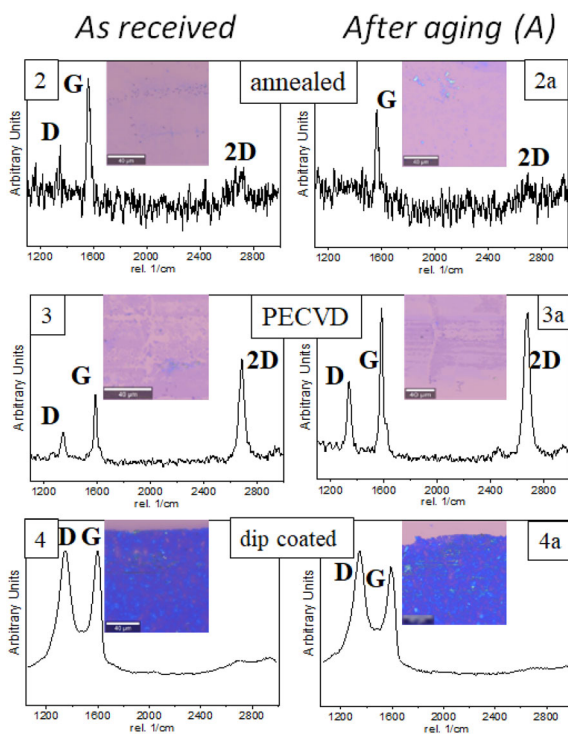


Fig. 5: Raman spectra of carbon material after transfer from Cu wires before (left) and after aging (right): (2) annealed, (3) CVD, (4) GO coated

aging, see Fig. 5. For samples 2 and 2a, small individual areas not larger than a few micrometers can be observed, which correspond to the SEM images from Fig. 3. For samples after the PECVD process, larger areas and clear peaks corresponding to multi-layer graphene can be observed. Damage to graphene is likely to result from the transfer process. The relatively extensive morphology and small diameter of the tested

wires limit the possibilities of perfect transfer of the graphene coating. After the dip coating process, the samples show a practically intact coating corresponding to a complete coverage, both before and after aging.

Defects in the coatings before and after the aging process are more visible in the Raman spectra maps, shown in Fig. 6. Colors in each image correspond to areas with Raman spectra corresponding to graphene and GO, whereas the black areas indicate the absence of coatings. The average spectra from the studied areas are presented on the left. Damaged graphene coating (3 and 3a) may be related to corrosion, and/or to damage resulting from the transfer process. The Raman spectra changes are aligned with the XPS results and show a partial degradation of the graphene coating. These changes are visible in the increase of the peak D intensity related to the sp^3 hybridization.

The maps indicate a significant durability of the GO layer after corrosion. In addition, negligible differences in the obtained spectra indicate its composition.

The durability of graphene material on the surface of the wires can be associated with its number of layers on the copper surface. To verify the number of layers of both graphene and GO on wires, a transfer to the TEM grids was performed. In Fig. 7, we can observe images of graphene (3), which point to the total coverage with a thickness of 2–3 atomic layers, along with local regions with more layers, resulting probably from the residual carbon on the surface of the wires from synthesis. Multilayer coverage (> 10 layers) in the case of GO (4) was observed.

Resistivity measurements

To assess the protective effectiveness of the graphene layers on the wires, resistivity measurements were performed. Table 2 shows the results of measurements at room temperature (20°C).

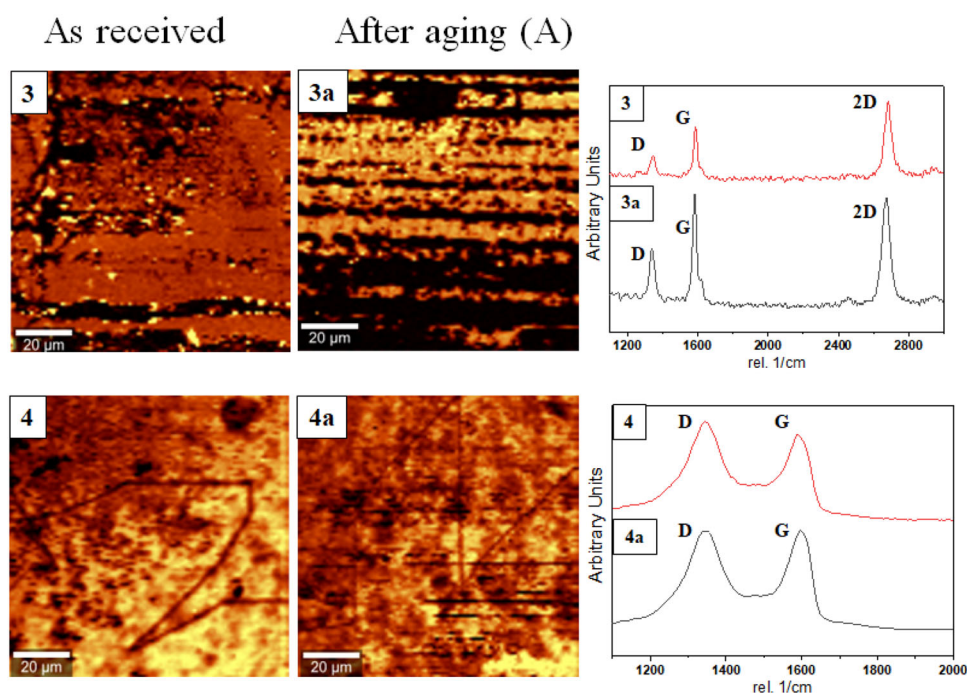


Fig. 6: Raman mapping area (left) and spectra (right) of graphene and GO before (3, 4) and after aging (3a, 4a) (Color figure online)

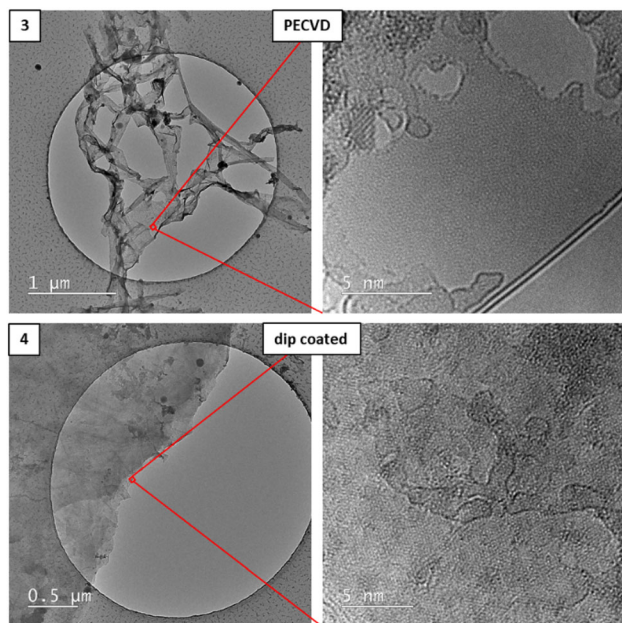


Fig. 7: HRTEM images of graphene (3) and GO (4) after transfer from samples after aging

Resistance measurements obtained from the wires prior to aging indicate that the conductivity deteriorates owing to the high-temperature processes for the annealed and PECVD coated wires.

The aging process indicates the protective properties for both the PECVD graphene and GO layer. After aging, the PECVD and dip coated wires show a lower increase in resistivity of 1.5 and 2.9 mΩ·cm, respectively, as compared to 4.3 and 4.4 mΩ·cm for washed and annealed wires, respectively. Furthermore, the commercially coated wire shows a greater resistance to corrosion than the unprotected wire with an increase in resistance after aging of 3.4 mΩ·cm.

The results of resistance tests conducted at elevated temperatures are shown in Fig. 8, both for wires before and after aging. In both cases, the resistance of the wire significantly increases with temperature after annealing. This is owing to the change in the surface morphology and crystal structure of copper. Samples coated with commercial varnish, GO, and PECVD graphene have similar changes in resistance. In addition, their resistivity is similar to the unprotected wire up to temperatures of 250°C. We can observe that PECVD graphene and the commercial coating have better protection against oxidation than coating with GO; however, these differences are insignificant. By comparing the annealed wire with the PECVD coated wire, we observed the greatest difference, indicating a considerable level of protection of the copper surface provided by graphene.

Figure 9 shows optical microscope images of samples subjected to resistance tests at elevated temperatures. They clearly demonstrate the nearly completely oxidized surfaces of the wires for the unprotected

Table 2: Results of resistance measurements at room temperature for wires before and after the aging process

	As recived [mΩ·cm]	After aging [mΩ·cm]	Increase of resistivity [mΩ·cm]
Washed	19.9	24.1	4.3
Annealed	24.2	28.6	4.4
PECVD	22.2	23.7	1.5
Dip coated	20.1	23.0	2.9
Commercial coating	24.8	28.2	3.4

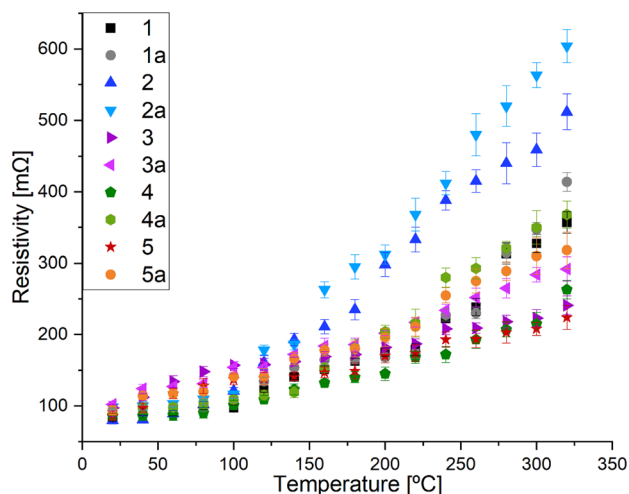


Fig. 8: Measurements of wires resistance at elevated temperature before and after aging

samples (1, 1a, 2, 2a) having a dark red to black color. The samples covered with graphene (3, 3a) have surfaces that are visibly protected against oxidation. The darker regions on the visible surface for wires coated with GO (4, 4a) and varnish (5, 5a) may be related both to copper oxidation and visualization of the protective layer itself.

Conclusions

We investigated the effect of the surface protection of copper wires by graphene coatings synthesized directly on the surface and applied from a solution. Thereafter, we compared the wire coated with graphene to commercial coated and unprotected wires. The degree of surface coverage and protection against salt mist and oxidation were assessed. This study experimentally proved the protective effectiveness of graphene layers with a thickness of 2–3 atomic layers for PECVD synthesis, whilst the possibility of protection by a relatively simple method of applying graphene oxide through dip coating was also identified. Microscopy images of the wire surfaces together with XPS showed the degree of surface protection clearly, which was particularly high for samples after the PECVD process. Raman spectra obtained for the transferred coatings

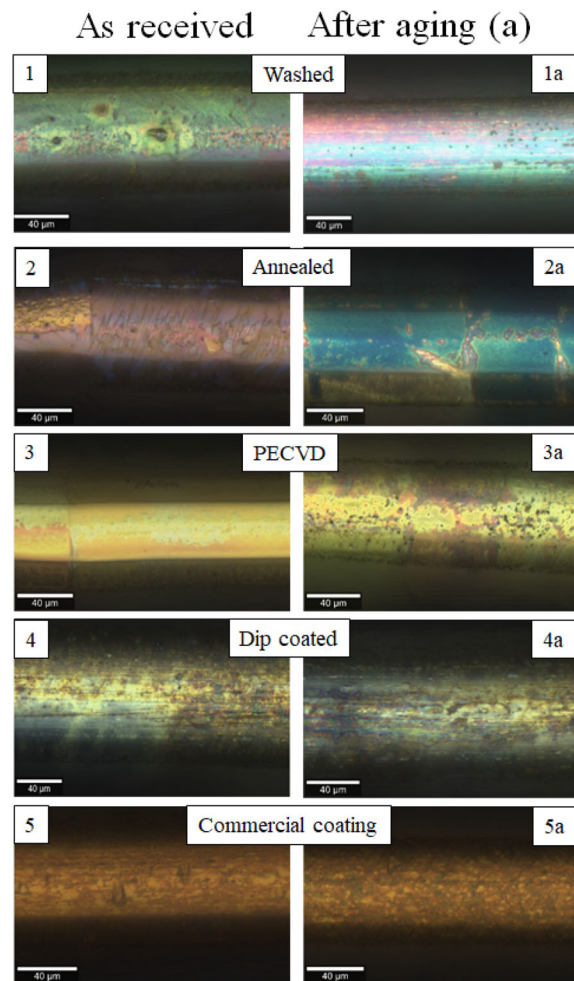


Fig. 9: Microscope images of Cu wires subjected to resistance tests at elevated temperatures, before (left) and after aging (right) (Color figure online)

demonstrated their structural stability, which indicates the possibility of using few atomic-layers-thick protective coatings for commercially available wires. Wire resistance tests showed similar or better results for graphene coatings than for commercially coated wires. The results of this study can be applied for further research on the mechanical suitability of the coatings and wires themselves, especially after high-tempera-

ture CVD processes. Such studies may lead to novel Cu wire processing technologies.

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