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Impact of electrolyte intercalation on the corrosion of graphene-coated copper

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ABSTRACT

The protection offered by graphene to copper mono- and polycrystals is studied. Cu(111) surface shows no traces of corrosion products due to the graphene coating. At the same time copper oxides are found on the copper polycrystalline foil despite the protection due to electrolyte intercalation at the graphene/copper interface. However, the amount of corrosion products is still lower in this case than in non-protected copper. The quantitative analysis of corrosion processes are based on XPS and AES spectra of non-coated and coated copper single and polycrystals. We evaluate graphene as a protection against corrosion in regard to industrial applications.

1. Introduction

Corrosion of copper is a major problem of the electronic industry. This metal, in its pure form, exhibits nearly unparalleled electrical and thermal conductivity values [1,2]. Those properties could ensure many applications of copper, such as interconnections, heat sinks or conductive tracks. However, during the exposure of copper surface to ambient atmosphere, a thin layer of oxides is formed in a series of electrochemical reactions [3–7]. The conductive properties of the corrosion products are significantly inferior to those of pure copper, and their presence on the surface drastically influences surface properties of the system [8,9]. In most cases this effectively limits the applicational potential of copper. Impact of the corrosion is especially important in the age of miniaturization of the electronic devices, as the changes in the structure of the surface influence properties of whole device.

There are various methods of controlling the corrosion of copper such as alloying or coating. Application of either of those methods might significantly reduce the scope of changes introduced by corrosion. However, such protection often comes at the price of the exceptional properties of copper – both alloying and coating may increase both electrical and thermal resistivity of copper [10]. Also, in case of coatings, the dimensions of the coated device are increased, as coating layers can have thickness of at least few nanometers. As each of those methods is useful in the narrow range of applications, one needs to put much care when alloying or coating copper.

Recently it has been shown that graphene can serve as impermeable barrier to molecules [11]. Because of this property it has been suggested to serve as the coating for various metals, including copper in both atmospheric and liquid conditions [12–16]. What is also important, graphene shows a degree of chemical inertness, therefore it not only protects the underlying surface, but also its structure remains unchanged during oxidation [17]. Moreover, graphene itself has unusual properties that in many cases cover those of copper. It has an excellent charge carrier mobility [18], thus may have no negative impact on the conductivity of graphene-coated copper devices. It is also excellent thermal conductor [19] and as such may not interfere with thermal properties of copper. As graphene can be easily grown as single or few layers it would not change the dimensions of copper devices. Furthermore, with the CVD method, graphene can be grown directly onto surface of copper, which simplifies the coating process and ensures high coverage [20]. It is also stable in air at the temperatures up to 500 °C [21]. Because of that graphene could prove to be an excellent coating agent for electronic applications of copper.

The CVD graphene grown directly on copper surface is not defect-free, however. Instead of single, continuous layer, it is composed of islands, or domains [22–24]. The barriers between them are usually not continuous or might have high defect density. The breaking of hexagonal symmetry of the lattice of graphene

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may serve as gateways for molecules and ions, thus lead to local corrosive changes in the chemical structure of copper [25]. Furthermore, different faces of copper crystals create different interfaces with graphene layers. In case of (1 1 1) face of Cu, the nearly identical atomic configurations of graphene and Cu(1 1 1) allow for no molecules of atmospheric gases or ions to intercalate between those two materials [26]. Interfaces of graphene and other faces of copper, however, do not inhibit that process in such degree [26].

Despite the fact that graphene-coated (1 1 1) single crystals offer the best corrosion resistance, polycrystalline copper is much more important from the point of view of applications of copper and it is dominant in industry. It is known, however, that the mismatched copper–graphene interface does allow for some degree of electrolyte intercalation between the two materials [27]. This leads to corrosive changes on top of the copper despite the protection. However, the quantitative characterization of this process faced significant difficulties. This is because the polycrystals are non-uniform and can differ in many aspects such as average copper grain size, which might impact the corrosion rate. For these reasons the efficiency of graphene protection for polycrystalline copper requires further investigations.

In this paper we try to address the issue of atmospheric corrosion in graphene-coated copper. We present the comprehensive results of our investigation of the corrosion of protected mono- and polycrystals in ambient conditions and compare the results to non-coated copper. We analyze the chemical structure of the samples after exposing to the atmospheric conditions. After confirming the crystallographic alignment and presence of the graphene layers in coated samples using Low Energy Electron Diffraction (LEED) and Raman Spectroscopy (RS) we investigate the changes in the chemical structure of the surface of the samples with complimentary techniques of Auger Electron Spectroscopy (AES) and X-ray Photoemission Spectroscopy (XPS).

Our investigations focus on assessment of the effectiveness of the protection against atmospheric corrosion in polycrystalline copper with graphene coating in comparison to most protected (1 1 1) surfaces and non-coated copper. We try to determine the importance of corrosion occurring in graphene-coated polycrystalline copper and the impact of this process in industrial applications.

2. Experimental

In this paper we present results of our investigations conducted on three samples. First of them was commercial copper single crystal with (1 1 1) oriented surface. This sample is later referred to as Cu(1 1 1). The second sample, referred to as G/Cu(1 1 1), was also a copper single crystal, however, the surface of the sample was coated with graphene. The sizes of both of those samples were 8 mm × 8 mm × 1 mm. The third sample was 8 mm × 8 mm × 0.2 mm polycrystalline copper coated with graphene. In this article it is referred to as G/Cu$_{foil}$.

The surfaces of Cu(1 1 1) and G/Cu(1 1 1), prior to coating with graphene, were prepared by electrochemical polishing to ensure desired orientation of the surfaces of the crystals. Subsequently all of the surfaces, including the substrate of G/Cu$_{foil}$, were cleaned under H_2/Ar gas flow at the pressure of 100 mbar at 1000 °C. Those conditions allowed for the contamination to desorb from the surfaces and for the reduction of the copper oxides formed by the corrosion that might have occurred beforehand.

The graphene coatings in G/Cu(1 1 1) and G/Cu$_{foil}$ samples were created with Chemical Vapor Deposition (CVD) method using a commercial horizontal CVD hot-wall reactor (Aixtron VP508), which is inductively heated with an RF generator, using propane (C_3H_8) gas as a precursor which was mixed with H_2 to limit sublimation of copper [28].

After the preparation of the samples, the Raman spectroscopy measures were conducted. Spectra were taken with Renishaw InVia spectrometer with 100× objective and 532 nm Nd:YAG laser light source.

All of the samples were exposed to the urban atmospheric conditions to enable the reactions of the corrosion. The influence of external phenomena, such as dust or wind, was minimized by a glass barrier. The exposure lasted 20 days. During that time the samples were held at the temperature of about 18–20 °C and atmospheric pressure. Humidity was close to 25%. During the exposure the amounts of NO_x species were estimated to about 24.7 $\mu g/m^3$ (including NO – 3.9 $\mu g/m^3$ and NO_2 – 18.6 $\mu g/m^3$), SO_2 to 9.3 $\mu g/m^3$ and CO to 457 $\mu g/m^3$.

After the mentioned exposure samples were analyzed in Ultra High Vacuum (UHV) conditions at pressure of $2 \cdot 10^{-10}$ mbar at room temperature in Omicron GmbH Multiprobe P system. LEED measurements were conducted with OCI LEED BDL800IR instrument. XPS and AES spectra were taken using Omicron NanoTechnology GmbH EA 125 hemispherical analyzer. XPS spectra were gathered with 0.05 eV step. The energy resolution of the analyzer was $\Delta E_A \approx 0.60$ eV. Non-monochromated Mg Kα (1253.6 eV, FWHM = 0.7 eV) radiation, generated with Omicron NanoTechnology GmbH DAR 400 source was used. For such parameters the resolution of XPS measurements (measured peak width) was close to $\Delta E_M \approx 1$ eV. In case of AES step of the spectra was 0.5 eV and the analyzer energy resolution was $\Delta E_A \approx 0.15$ eV. 3 keV electron beam was generated with Omicron NanoTechnology GmbH EKF 300 source. The size of the spot was 500 μm.

3. Results and discussion

To verify starting parameters of the test samples we identified the crystallographic structure and the presence of graphene in the investigated samples. For that purpose we used LEED and RS techniques, the latter was conducted only on graphene-coated samples.

The LEED pattern of Cu(1 1 1) sample is shown in Fig. 1(a). It consists of six spots forming a hexagon around zero-order diffraction point. It originates from the lattice of (1 1 1) surface of copper crystal [29].

The diffraction pattern of G/Cu(1 1 1) sample is presented in Fig. 1(b). It is significantly different from that of Cu(1 1 1). Three sets of spots are visible, indicated by the red and blue hexagons. The inner, red hexagon corresponds to the surface of copper. The outer spots are connected by a ring, the presence of which indicates that there is a degree of disorder in the orientation of graphene domains in the coating [26,30]. Two of the orientations are favored because of the influence of the lattice of the substrate on the growth of the CVD graphene [31].

The structure of the LEED pattern of G/Cu$_{foil}$, as seen in Fig. 1(c) is different from the previous samples. The pattern of the copper substrate is not visible. All of the symmetrical features of the image correspond to the graphene coating. As was the case for G/Cu(1 1 1), here we also see the ring indicating the disorder in the graphene domain orientations. In the pattern of G/Cu$_{foil}$ we can also see that there are three preferred orientations of the graphene domains rotated relative to each other by 7°. Such configurations were also observed by other groups [32]. We believe that those may suggest that areas where coating is thicker than single atomic layer might be present.

The Raman spectra of G/Cu(1 1 1) and G/Cu$_{foil}$ are shown in Fig 1(d). The presence of both G and 2D peaks confirm graphitic carbon presence on surface of both samples. The 2D/G intensity ratio is