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Wettability effect of graphene-based surfaces on silicon carbide and their influence on hydrophobicity of nanocrystalline cerium oxide films

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ABSTRACT

We investigate the water-repellent ability of graphene-based surfaces stabilized on silicon carbide (SiC) and the nanocrystalline cerium oxide (CeO_2) films electrodeposited on them. Water contact angle is revealed strongly dependent on the number of graphene monolayers on SiC, indicating partial permeability of graphene on SiC. Fluctuations in the roughness of textured surfaces as well as variations of oxygen vacancy content in CeO_2 electrodeposits are determinant for the hydrophobicity of the interaction between water droplets and nanocrystalline CeO_2 electrodeposits on monolayers graphene on SiC.

1. Introduction

Wetting ability can be described as the ability to bond or adhere between solid and liquid phases at the point of interfacial contact. The degree of contact at the solid/liquid interface is a result of adhesive and cohesive forces whose primary cause is the intermolecular interactions between solid and liquid.

The contact angle quantifies the wettability of a solid surface by a liquid via the Young equation [1]. During wetting, the liquid can spread across the solid surface in case of strong adherence or cause a liquid drop to ball-up, avoiding as much contact as possible in case of weak wettability. A surface is more wettable when the surface tension is low and when the contact angle is low. In a hydrophobic interface the contact angle value exceeds 90°, with the formation of a compact liquid droplet.

The contact angle can be influenced by various experimental parameters, including variation in exposure time and temperature as well as surface substrate conditions. Interfacial reactions are strongly dependent on the chemistry, structure, and topography of the contact area [2]. Because the carbon lattice is perfectly nonpolar, clean graphite and graphene surfaces have long been regarded as hydrophobic, with contact angles $\sim 92°$ [3,4]. However, a slightly hydrophilic nature of the graphite (and graphene) was recently reported [5]. The exposure to air-born hydrocarbons was pointed out as the cause of the appearance of hydrophobicity. Nevertheless, both the effective geometric superficial area and surface roughness of graphene remain open issues with strong impact on the contact angle at the interface between water and graphene surfaces on a substrate.

Recent approaches employ thermal sublimation of SiC substrate under argon at atmospheric pressure or under Si flux [6–8] as well as ultrahigh-vacuum graphitization to obtain higher quality graphene and graphite surfaces [9,10]. The bottom-up growth of graphene on SiC surfaces occurs by sublimation of Si atoms via SiC atomic steps and through the interfacial carbon layer, with subsequent formation of few graphene layers, resulting from the additional sublimation of Si atoms and structural defect-assisted mechanisms.

These kinds of graphene-based surfaces are excellent templates to investigate the water wettability because their typical morphology varies from terraces measuring a few micrometers up to undisturbed, atomically flat terraces, extending over 50 mm in length. Apart from corrugations, ripples, wrinkles, and ridges, the structural defects are only delimited by the substrate terraces and steps [9]. Because this, the underlying SiC surface preserves their characteristic structure and smoothness.

CeO_2–graphene hybrid nanocomposites have attracted much attention due to their performance as supercapacitors [11] and for many technological applications including catalytic converters, luminescent panels, fuel cells, and solar cells [12–15] as well as in

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electrochemical and biomedical sensors [16–18]. In this work, we investigate the wettability effect of graphene-based surfaces stabilized on SiC wafers and their influence on the hydrophobicity of electrodeposits of CeO_2, a rare-earth oxide belonging to the lanthanide series, which was recently revealed as having intrinsically superhydrophobic surface [19].

2. Experimental

We used SiC(0001) wafers exposed to hydrogen etching at 1600 °C in order to remove polishing damages, subsequently annealed under a Si flux at 900 °C to remove the native oxide. Further annealing at temperatures higher than 900 °C induces the gradual development of monolayer growth of graphene due to Si depletion towards a partially graphitized surface [6,10]. These substrates were used in the present experiment as templates to electrodeposition of thin stoichiometric and non-stoichiometric CeO_2 films using the potentiostatic method with a potentiostat/galvanostat (EG&G model 273A). The CeO_2 films were cathodically electrodeposited at room temperature using a stationary three-electrode cell. A standard saturated Ag/AgCl electrode was used as the reference electrode, while a platinum disk was used as the counter-electrode. CeO_2 films were deposited from bi-distilled aqueous solutions containing 0.8 mmol/L of $CeCl_3 \cdot 7H_2O$ with and without the addition of 20 mmol/L of hydrogen peroxide (H_2O_2) at cathodic potentials of -1.0 and -1.2 V, respectively, versus a Ag/AgCl reference electrode. Deposits less defective in oxygen are attained from solutions containing H_2O_2 additive. Whereas the pH value remains 5.6 in the absence of additive, the addition of H_2O_2 leads to solutions with pH values of 3.5. The working electrodes were ultra-high vacuum graphitized SiC wafers with areas between 1.0 and 0.5 cm^2. CeO_2 films were also deposited on Si(001) wafers as described elsewhere [21,22].

In order to monitor the stoichiometry of CeO_2 films we performed X-ray photoelectron spectroscopy (XPS) measurements using a VG ESCA3000 spectrometer equipped with a conventional Mg X-ray source and a hemispherical energy analyzer with an overall resolution of 0.8 eV at 45° emission angle.

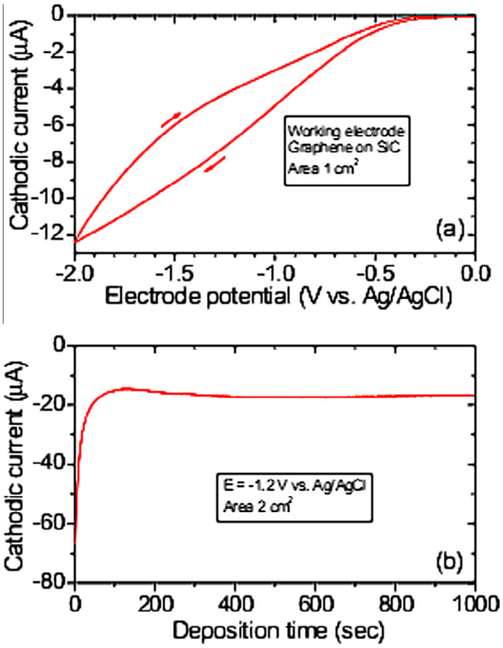

Fig. 1. (a) Cyclic voltammogram of graphene/SiC electrode in aqueous cerium chloride solution at scan rate of 50 mV s^{-1} and (b) chronoamperometric curve during CeO_2 electrodeposition on graphene/SiC substrates.

All the electrodeposits showed no evidences of Bragg reflection in the X-ray diffraction measurements, indicating their nanocrystalline structures. The samples surface morphology was determined using a Shimadzu SPM 9500 atomic force microscope operating in tapping mode.

Confocal Raman microspectroscopy analyses were performed using a Witec alpha 300R confocal optical microscope which can perform selective chemical imaging with spectrometric resolution of 0.02 cm^{-1}. A 532-nm laser collimated by a 100× air objective was used for excitation.

The wetting experiments were performed at 25 °C using a Data Physics model OCA 15plus tensiometer (Filderstadt, Germany). The static sessile drop method was used for the contact angle measurement. The fluid medium used in the measurements of the contact angle was ultrapure water. Droplet volume was controlled with an automatic dispensing system containing a 500-μL Hamilton syringe (Bonaduz, Switzerland), a needle with an internal diameter

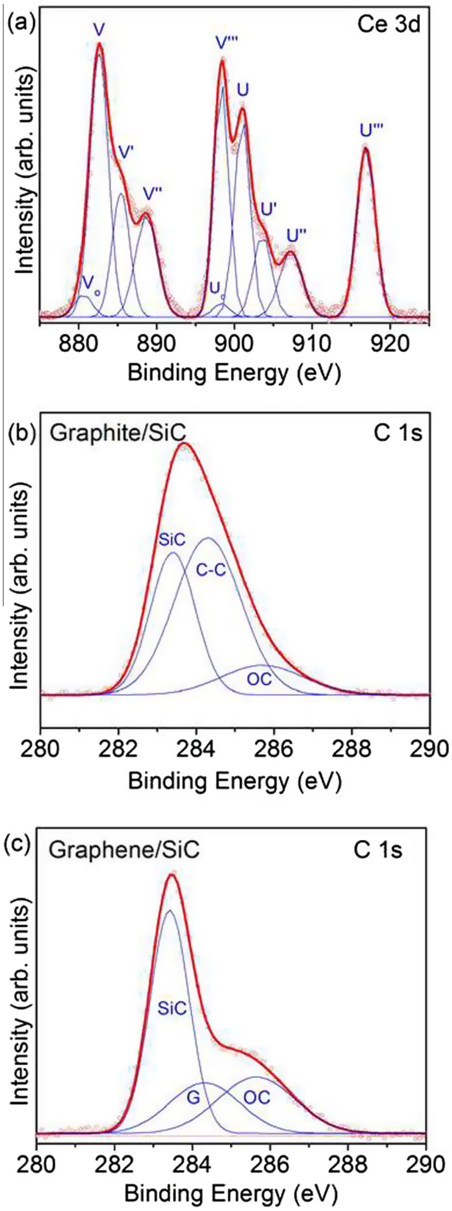

Fig. 2. (a) Ce 3d XPS spectrum after background substraction with deconvolution and assignments of five pairs of doublets used to estimate the relative Ce^{3+} with respect to Ce^{4+} sites which reflects the amount of oxygen vacancies. C 1s XPS spectra for graphite (b) and graphene (c) surfaces grown on SiC substrates. Contributions of SiC, graphene *G*, and oxycarbides OC bands are observed.