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Graphene on silicon carbide as a basis for gas- and biosensor applications

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The structural, chemical, and electronic characteristics of graphene grown by thermal decomposition of a singlecrystal SiC substrate in Ar atmosphere are presented. It is shown that this technology allows the creation of high-quality monolayer graphene films with a small fraction of bilayer graphene inclusions. The performance of graphene on SiC as a gas sensor or a biosensor was tested. The sensitivity of gas sensors to NO_2 on the order of 1 ppb and that of biosensors to fluorescein with concentration on the order of 1 ng/mL and to bovine serum albumin–fluorescein conjugate with concentration on the order of 1 ng/mL were determined.

Keywords: graphene, silicon carbide, thermal decomposition, Raman spectroscopy, AFM, XPS, ARPES.

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1. Introduction

Graphene is a promising material with unique properties, such as high surface-to-volume ratio, low electrical noise, and exceptional transport properties associated with its two-dimensional structure [1]. One of the most promising techniques for graphene synthesis, which can be integrated into industrial production, is the thermal decomposition of the surface of semi-insulating silicon carbide (SiC) substrates [2]. The main advantages of this method are the high structural perfection of the resulting graphene films and the possibility of growing a graphene film on a semi-insulating substrate. In this paper, we present the results obtained in the study of the characteristics of graphene films grown by thermal decomposition on the SiC surface and in the performance test of graphene as a gas sensor and a biosensor.

2. Experimental

Graphene films were grown by thermal decomposition of single-crystal semi-insulating $6H$-SiC and $4H$-SiC substrates under Ar at 1800–1850 °C over 10 min. The growth was carried out on the Si-face [SiC (0001)] of a substrate. Before synthesis, organic and inorganic solvents were used to clean the substrate surface. The structural, chemical, and electronic characteristics of graphene were monitored by Raman spectroscopy, atomic force microscopy (AFM), X-ray photoelectron and angle-resolved photoemission spectroscopy (XPS and ARPES).

3. Results

Raman spectroscopy and AFM were used to determine the thickness uniformity of a graphene film. Fig. 1a presents an array of Raman spectra measured in the range of 1300–2800 cm^{-1} at a sample area of 12.5×12.5 μm^2. An analysis of the G line intensity map obtained by processing this array revealed a quite uniform distribution of the line intensity. This suggests that the graphene film has good thickness uniformity in the area being analyzed. It was found that the $2D$-line is symmetric in most of spectra and is well fitted by a single Lorentzian, which is a fingerprint of the single-layer graphene [3]. Fig. 1b shows the map of the surface potential distribution, furnished by Kelvin probe microscopy. It was found that the potential difference between the light and dark areas

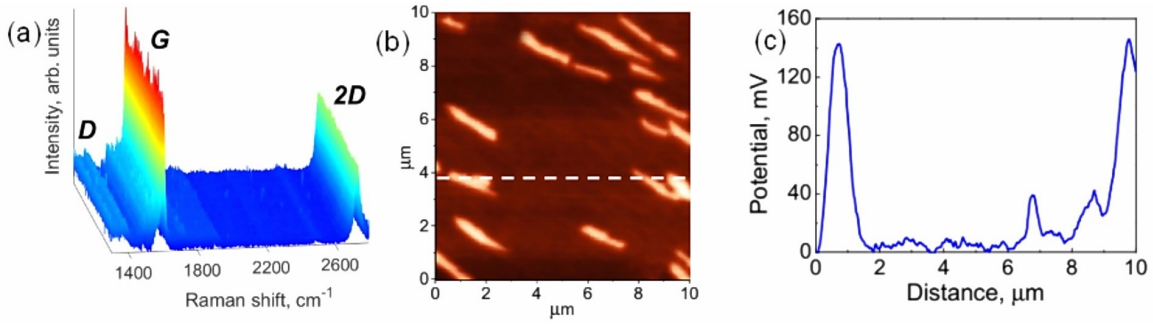

FIG. 1. Array of Raman spectra for a sample grown on the Si face of 6H-SiC (a). Surface potential distribution (b) and the corresponding profile (c)

is ∼140 mV (Fig. 1c). This value corresponds to the surface potential difference between one- and two-layer graphene [4].

In order to reliably determine the thickness of graphene, XPS spectra were measured at four photon energies, which provided different depths of analysis in the range 5–23 Å. The layer thickness was determined by choosing the thicknesses of graphene and the buffer layer that ensured the best match between the calculated and measured intensities of individual components of the C 1s spectra. The results are shown in Fig. 2c, which presents relative intensities for the optimal thicknesses, i.e., 3.3 Å for the buffer layer and 5.5 Å for graphene. This corresponds to 1.0 and 1.6 carbon sp^2 layers for the buffer layer and graphene, respectively. The ARPES data representing the electronic structure of the valence band of the graphene/SiC(0001) system are shown in Fig. 2b. An unsplit Dirac cone indicating that a single-layer graphene coating dominates on the surface is seen at the K point.

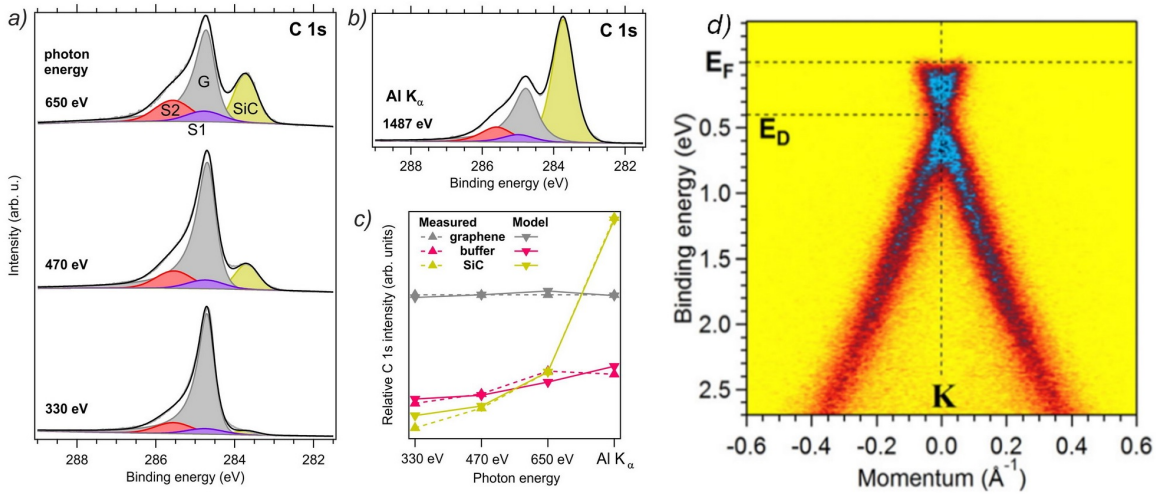

FIG. 2. XPS spectra measured in the C 1s region at various photon energies (a, b). Intensities of individual spectral components, compared with the results of simulation (c). ARPES map of the valence band at the Kpoint of the Brillouin zone ($h\nu = 40.8$ eV) (d)

In order to perform surface sensitivity measurements of graphene films on SiC, a sensor structure with Ohm contacts was fabricated. The sensor topology was provided by photolithography over AZ5214 resist. The reactive ion etching in argon and oxygen plasma was used to remove the graphene layer from uncoated areas A Ti/Au metallization was used to fabricate Ohm contacts.

To measure the sensitivity of a sensor for gas detected in dry air, gas-mixing and gas-supplying system was used. The operation of the gas sensor was tested with NO_2 present in low concentrations in dry air. The sensor sensitivity $r$was determined as the relative change of sample resistance in presence of a gas recorded in the gas mixture:

$$r = \frac{R - R_0}{R_0}. \tag{1}$$

Here, R is the resistance of the sensor exposed to the gas mixture, and R_0 is the initial resistance in the absence of the gas to be detected in the incoming air flow.

Figure 3a shows the response of a graphene sensor exposed to a gas mixture containing NO_2 gas at 20 °C It can be seen that the NO_2 concentration as low as 0.5 ppb is easily detectable.

The working capacity of the biosensor was tested against an immunochemical system constituted by fluorescein and monoclonal antibodies (mAbs) binding this dye. The antibodies were attached to the graphene surface via amino groups formed by a number of electrochemical reactions. The biosensor was placed in a buffer borate solution to which fluorescein molecules were added. The attachment of fluorescein molecules to the antibodies situated on the graphene surface changed the total resistance of the graphene film. It was found that the sensor detects a fluorescein concentration on the order of 1–10 ng/mL (Fig. 3b) and a concentration of conjugate of bovine serum albumin with fluorescein on the order of 1–5 ng/mL (Fig. 3c).

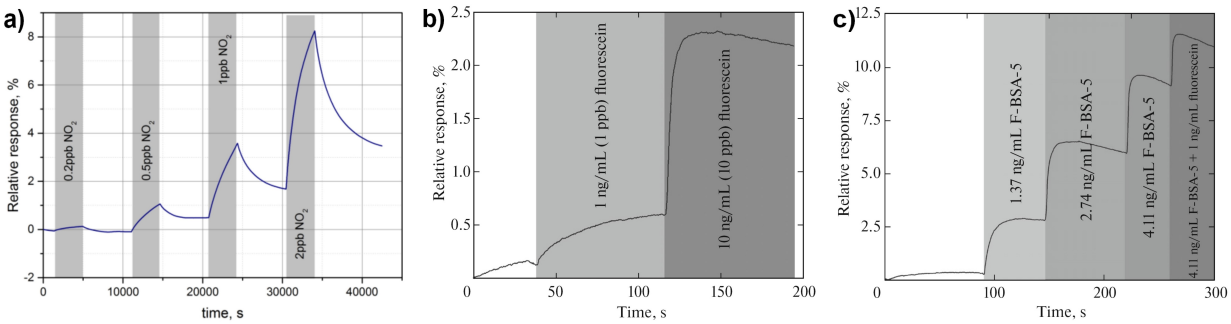

FIG. 3. Response of a graphene sensor exposed to (a) the gas mixture containing NO_2 gas, (b) solutions containing free fluorescein (at indicated concentrations), (c) solutions containing BSA–fluorescein conjugate (F-BSA-5) or a mixture of this conjugate with free fluorescein (at indicated concentration)

4. Conclusion

Graphene films grown by thermal decomposition of SiC under argon and the application of these films as a gas or a biosensor were studied. It was found that this technology allows the synthesis of high-quality monolayer graphene films with a small fraction of bilayer graphene inclusions. Tests of gas sensors and biosensors based on SiC-supported graphene films showed an extremely high sensitivity to detectable substances. These results demonstrate that the graphene growth technology on SiC is promising for development of next-generation sensors.

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