Growth and electronic structure of graphene on semiconducting Ge(110)

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A B S T R A C T

The direct growth of graphene on semiconducting or insulating substrates might help to overcome main drawbacks of metal-based synthesis, like metal-atom contaminations of graphene, transfer issues, etc. Here we present the growth of graphene on n-doped semiconducting Ge(110) by using an atomic carbon source and the study of the structural and electronic properties of the obtained interface. We found that graphene interacts weakly with the underlying Ge(110) substrate that keeps graphene's electronic structure almost intact promoting this interface for future graphene-semiconductor applications. The effect of dopants in Ge on the electronic properties of graphene is also discussed.

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1. Introduction

Presently, the main synthesis methods of graphene (gr), a purely 2D material consisting of carbon atoms, which can be scaled down in order to be used in further applications, are its preparation on semiconducting SiC [1–3] or on metallic substrates [4–7]. However, these methods have natural drawbacks like, e. g., the price of the high-quality SiC wafers and very high processing temperature ($T > 1300°$ C) used for the growth of the uniformly monolayer-thick homogeneous graphene on SiC [2,8]. In the case of graphene synthesis on metal substrates with subsequent transfer onto the desired support, it was found that the level of metal-atom contamination in the obtained graphene is not acceptable for modern microelectronics [9,10]. These as well as other fundamental problems limit the commercialization of graphene [11,12] and stimulate researchers to search for new ways of graphene synthesis.

One possibility to implement graphene in modern microelectronics processing is to perform its synthesis directly on an insulating substrate. Here one option is to use h-BN, which can be grown on the metallic substrates, like Cu, Fe, or Ni, or on semiconductors, like Ge, thus allowing a chemical vapour deposition (CVD) synthesis of graphene, furthermore to produce a tunnel barrier for the carrier injection in graphene, and to avoid a metal contamination of graphene [13–15]. Another approach implies a direct growth of graphene on the technologically relevant SiO_2/Si(001) substrate, that was successfully demonstrated recently [16].

A different method comprises graphene synthesis directly on a semiconducting substrate. The direct growth of graphene on Si is problematic due to its carbidic phase formation at high temperatures [17–21]. However, the recent progress in graphene synthesis reveals the possibility to grow single- and multilayer graphene on Ge and Ge/Si substrates [22–26]. While the Ge(001) surface is the most technologically relevant one, a faceting of the underlying Ge with the Ge(107) facets upon graphene growth was found by means of scanning electron and tunneling microscopy (SEM and STM) [25,27,28], which limits further technological processing of this interface. In contrast to the previous case, graphene as well as the underlying Ge surface remain flat for the Ge(110) surface, which was confirmed by low-energy electron diffraction (LEED) and STM [22,24,25]. Despite the availability of a number of intensive studies on the growth of graphene on Ge, little is known about the electronic structure of this interface [29]. In this work, the *ex situ* CVD

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grown graphene flakes on undoped Ge/Si(001) were investigated by means of micro- and nano-ARPES (angle-resolved photoelectron spectroscopy), which indicates the free-standing character of graphene maintaining the linear dispersion of the π states in the vicinity of the Fermi level (E_F) and its p-doping with the position of the Dirac point of $E_D = 0.185$ eV above E_F.

Here we present a complete *in situ* UHV preparation as well as a structural and electronic properties study of a graphene layer epitaxially grown from an atomic carbon source on Ge(110). The presented LEED and STM results confirm the high quality of the prepared system indicating the existence of a reconstructed Ge(110) surface below graphene. Our x-ray photoelectron spectroscopy (XPS), normal-emission ARPES (NE PES), and energy-loss near-edge spectroscopy performed at the carbon K-edge (C K-edge ELNES) reveal the nearly free-standing behaviour of graphene on Ge(110). We also address the plasmon excitations in this system performing electron-energy loss spectroscopy (EELS). Our results were compared and analyzed with the available theoretical spectroscopic data for free-standing graphene and "strongly-interacting" gr/Ni(111) demonstrating good agreement with the former case.

2. Experimental details

Growth of graphene and all studies were performed in the surface science cluster tool (Omicron NanoTechnology; base pressure 1×10^{-10} mbar). Prior to every experiment a Ge(110) substrate (G-materials (Germany), Sb doped, resistivity $0.35\ \Omega\cdot$cm) was cleaned via cycles of Ar$^+$-sputtering (1.5 keV, $p(\text{Ar}) = 1 \times 10^{-5}$ mbar) and annealing ($T = 870^\circ$ C). Graphene was grown on the hot Ge(110) substrate ($T = 860 - 870^\circ$ C) from an atomic carbon source (Dr. Eberl MBE-Komponenten GmbH) with a filament current of $I = 70$ A and maximum pressure of 2×10^{-9} mbar during C-deposition. The cleanliness and quality of the samples was controlled by LEED, STM (Omicron VT-SPM), NE PES (non-monochromatized He II line), and XPS (non-monochromatized Al K line; energy analyzer Omicron EA 125 was set either in angle-resolved or in angle-integrated mode, respectively) after every preparation step. ELNES and EELS experiments were performed in the specularly-reflected electron beam mode with angular and energy resolution of 1° and ≈ 1 eV, respectively. The primary electron energy is marked for every spectrum. Low-temperature (LT) STM experiments were performed in an Omicron Cryogenic STM on the gr/Ge(110) sample quickly transferred from the growth/characterization facility under N$_2$-atmosphere. Following the transfer, gr/Ge(110) was annealed in UHV at 700° C.

3. Results and discussions

The growth of graphene on Ge(110) was characterized by means of STM, LEED, and XPS and these results are compiled in Figs. 1 and 2. The Ge(110) surface shows a large scale ordering as can be deduced from the STM [Fig. 1 (a,b)] and LEED images [Fig. 1(f)]. According to previous studies this surface can be described as a faceted surface with {17 15 1} facets and $c(8 \times 10)$ reconstruction on the steps [30–33]. Deposition of carbon on Ge(110) at $T = 870^\circ$ C and subsequent cooling of the sample to room temperature lifts the previously observed reconstruction, however, producing an ordered underlying Ge surface as can be seen from the respective STM and LEED images [Fig. 1(c–e,g)].

The prepared graphene layer forms two types of domains rotated by 30° with respect to each other as seen from LEED and demonstrates a clear honeycomb sp^2 structure on the Ge(110) surface [Fig. 1(c–e,h)]. Our results on the observation of two graphene domains are consistent with the previously reported data for

CVD grown graphene on Ge(110) [25]. The observed alignment of the graphene lattices of the two domains differs by $\approx 15^\circ$ compared to the one observed for the single-domain graphene growth in Ref. [24]. Similar to the results presented in this reference, our growth method rules out the influence of hydrogen on the alignment of graphene on Ge(110); however, further structural studies, are required.

STM experiments performed on the large scale [Fig. 1(c and d)] and at different bias voltages [Fig. 1(e)] allow to obtain information on the thickness of a graphene layer and to resolve the atomic structure of graphene and the Ge(110) substrate underneath. A horizontal height profile taken across the STM image presented in panel (d) yields a height difference of ≈ 3.2 Å between the clean and graphene covered Ge(110) surface. This value is in very good agreement with the graphene–Ge-adatom distance of ≈ 3 Å obtained in the recent density functional theory (DFT) calculations for this system [24]. An average height of $3.7 - 3.8$ Å between the graphene sheet and Ge(110) surface atoms was obtained in these calculations. The discussed experimental facts (possibility to measure LEED of the underlying reconstructed Ge(110) surface; measured height profile agrees with the theoretical value; possibility to discriminate between graphene and Ge(110) in STM experiments depending on the tunneling bias voltage) confirm our conclusion about the monolayer-thick graphene patches on Ge(110) in our samples.

Our atomically resolved STM images demonstrate clear signatures of quasiparticle scattering in the graphene layer due to imperfections in graphene as well as due to the presence of the scattering centres at the interface (segregated dopants, see discussion below). The interference of the scattering waves of the carriers in graphene leads to the formation of the corresponding $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with respect to the graphene atomic-related structure in the 2D Fast-Fourier-Transformation (FFT) map. The spots of these structures are marked in the upper inset of Fig. 1(e) by white rectangle and circle, respectively. This $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure in the FFT map is assigned to the so-called intervalley scattering between adjacent cones at the K and K' points of the graphene-derived Brillouin zone.

The Raman spectrum of one of the gr/Ge(110) samples with an estimated graphene coverage of $\approx 50 - 60\%$ is presented in Fig. 1(i). All graphene-related spectral features ("2D", "G", "D") are clearly resolved (the peak at 2329 cm^{-1} and the weak shoulder at 1556 cm^{-1} are due to atmospheric oxygen and nitrogen [23]). The 2D peak can be fitted with the single Lorentzian function: peak position 2725 cm^{-1} and FWHM = 65 cm^{-1}. The relatively low 2D/G intensity ratio indicates the formation of graphene patches on the Ge(110) surface. The observed high intensity of the D peak also hints towards the patch-like structure of our graphene sample on Ge(110) with a large contribution of the flake edges in the resulting Raman signal.

The formation of the uniform graphene sp^2 structure is also confirmed by XPS data (Fig. 2). High-temperature deposition of graphene on Ge(110) only leads to a damping of the Ge 2p XPS signal [Fig. 2(a and b)] without any indication of the formation of Ge–C bonds as can be concluded from the analysis of the Ge-related XPS peaks. Our data reveal a single C 1s peak for gr/Ge(110) with a small shoulder at a low binding energies (due to the possible bonds between carbon atoms and dopant atoms segregated at the interface) that confirms the homogeneity of the prepared gr/Ge(110) system.

The electronic structure of the grown graphene layer on Ge(110) was investigated by NE PES for the occupied valence band states below E_F and by C K-edge ELNES for the unoccupied states above E_F and these results are presented in Fig. 3(a and b), respectively. From the comparison of the PES spectrum of gr/Ge(110) with the one of a