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Graphene-induced Ge (001) surface faceting

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ABSTRACT

Faceted Ge surfaces result from the growth of a graphene overlayer on Ge (001) by chemical vapor deposition. The surface exhibits four-fold symmetry after faceting, with the surface normal of the facets tilted towards [100] from the average surface normal. X-ray reflectivity measurements allow the facet angles, directions, and symmetry to be measured precisely as a function of deposition conditions. Graphene grown from a CH_4 precursor in a H_2/Ar carrier atmosphere at temperatures from 870 to 920 °C yields facets on the Ge surface with an average facet angle of 7.70° ± 0.07°. Additionally, a distribution of facet angles is observed with an angular spread of approximately ±1°. The facet pattern has four-fold symmetry over a large area with no indication of the formation of competing facets from reflectivity measurements. The facet angle tends toward the {107} facet of Ge with slight variation as a function of temperature indicating that the facet angles are dominated by surface energetics. The slight dependence on temperature is accompanied by a reconstruction of the surface into {001} facets under slow-cooling conditions, suggesting that the surface diffusion kinetics and temperature dependence have an important role in the formation of the faceted surface structure at lower temperatures.

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1. Introduction

The formation of surface facets provides insight into the chemistry and energetics of crystal surfaces and their interfaces with other materials. The faceting of an initially planar surface occurs through a process of nanometer scale self-assembly that exposes new crystal faces and creates additional surface area [1]. While surface faceting is ultimately driven by a minimization of the total surface free energy, the evolution of the surface upon, for example, the creation of interfaces, is controlled by kinetic processes including nucleation and diffusion [1]. By studying the surface geometry and processing conditions that lead to faceting, it is possible to examine the interplay between thermodynamics and kinetics in complex interfacial systems. Although faceting phenomena have most often been observed with atomic or molecular absorbates, recent observations have found that faceting can also occur during the formation of two-dimensional materials.

In particular, the formation of Ge facets below graphene grown on Ge (001) via chemical vapor deposition was recently reported [2]. These Ge facets form during the deposition of graphene at elevated temperatures and are stable under ambient conditions after rapid cooling to room temperature [2]. The faceting is highly selective, as it only occurs in areas where graphene has nucleated and is even observed below relatively small crystals with dimensions less than 10 nm. Atomic force microscopy shows that the Ge/graphene faceting pattern exhibits four-fold symmetry, with approximately equal area occupying each of the four facet domains [2]. The nanometer-scale structure of the faceted Ge/graphene surface is clear from scanning tunneling microscopy studies, which show that the facets are stable under ambient conditions and upon reintroduction into vacuum [2]. These Ge facets belong to the {10 L} family. Interestingly, such faceting was not reported in other studies of graphene growth on Ge (001), which may be due to differences in growth conditions, differences in the thermal profile, or the absence of characterization of the Ge surface [3,4].

The formation of {10 L} facets has been previously observed on Ge surfaces under a number of conditions. The heteroepitaxial growth of elastically strained Ge with a thickness of a few atomic layers on Si (001) results in the formation of Ge islands with {105} facets, allowing the elastic relaxation of the near-surface region and lowering the total strain energy [5,6]. The Ge {107} facet is formed as a result of mounding in Sn-mediated Ge/Ge (001) homoepitaxy [7]. Contributions to the relative energetic stability of facets on Ge include the atomic reconstruction of the faceted surface and the strain dependence of the Ge surface energy [6,8].

Here we report a systematic x-ray reflectivity study of the formation of facets below continuous graphene films grown on Ge (001) by chemical vapor deposition. Unlike atomic force and scanning tunneling microscopy measurements, x-ray scattering provides precise insight into the orientation and roughness of the facets over large areas and thus provide precise statistical averages for the faceted surface structure. The creation of multiple surfaces with different orientations splits the surface diffraction spots in surface x-ray diffraction and reflectivity, producing multiple crystal truncation rods [9]. For an accurately oriented high-index surface, each truncation rod passes through both the origin of reciprocal space and a series of Bragg reflections. With small

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misorientations, the origin and each Bragg reflection produce a rod of intensity at a specular angle depending on the misorientation [9]. At the small angles of x-ray incidence on which we focus here, the specular reflection from the surface is thus split by the pattern of facets [10]. In the limit of the x-ray beams with short transverse coherence lengths produced by laboratory x-ray sources, the scattering pattern of surfaces with multiple facets can be accurately approximated as the appropriately weighted sum of the intensities of a series of misoriented surfaces. X-ray reflectivity studies of faceted surfaces have included step-driven faceting in Si [11–13], faceting in Au [14] and Pt [15], and earlier studies on Cu surfaces [10]. In a technical sense, the results reported here extend x-ray reflectivity methods to the special case of Ge/graphene and describe the analysis methods necessary to perform such studies using large two-dimensional x-ray detectors.

Understanding the surface energetics and interactions of the Ge/graphene system is also important to advance the synthesis of graphene on semiconducting substrates, and in ultimately promoting better compatibility of graphene with conventional microelectronics [2,3]. The formation of facets during the synthesis of graphene nanoribbons on Ge (001) is particularly interesting, as this growth process has the potential to lead to arrays of high-quality semiconducting nanoribbons directly on a substrate compatible with conventional microelectronics. An improved understanding of the thermodynamics and kinetics of the Ge/graphene system will help lead to increased structural control during the creation of graphene nanoribbon arrays and continuous graphene sheets, and will enable expansion of this insight to growth procedures for other monolayer/substrate combinations.

2. Experimental conditions

The faceting of the Ge surfaces was investigated using Ge/graphene samples grown at temperatures of 870 °C, 910 °C, and 920 °C at atmospheric pressure using 4.6 sccm of CH_4 as the carbon precursor and a mixture of 200 sccm of Ar and 100 sccm of H_2 as the reducing carrier gas. Growth times of 42, 12, and 10 h were used for synthesis at 870 °C, 910 °C, and 920 °C, respectively, to ensure that a continuous layer of graphene covered the entire surface. Following growth, the samples were rapidly cooled in the same environment used during synthesis by sliding the furnace away from the growth zone to bring the samples to room temperature. This process resulted in complete coverage of the surface by a single layer of graphene distributed across hill-and-valley facets [2]. Fig. 1(a) and (b) show SEM and AFM images, respectively, of the local surface faceting of the Ge under the graphene. The dimensions of the faceted structure visible in the SEM and AFM images are typically less than 6 nm high and nearly 70 nm wide, valley-to-valley, along their short axis. The ridges between facets are nearly parallel to the <100> directions. The faint ripples visible in the AFM image in Fig. 1(b) arise from wrinkling of the graphene during cooling as a result of the mismatch in the thermal expansion coefficients between graphene and Ge. Interestingly, graphene growth followed by a much slower cooling rate of 0.5 °C/min results in a different Ge faceting motif, which will be discussed in more detail below.

A systematic precise study of the faceting angles was performed using x-ray reflectivity. The Ge/graphene surface produces specular x-ray reflections from the facets that form during the growth of the graphene layer. Reflectivity measurements can be interpreted with geometric optics in methods similar to previous studies of faceting of Si surfaces [12,16]. These methods must be adapted for the use of large-area two-dimensional x-ray detectors that permit the collection of intensity data from multiple surface truncation rods simultaneously.

X-ray reflectivity measurements were performed with a Bruker D8 Discover with a VÅNTEC 500 Area Detector in a theta–theta geometry with the detector subtending an opening angle of 39°. A Bruker IμS microfocus x-ray source was operated at 50 W to produce a Cu kα incident x-ray beam with a flux estimated to be 2.3×10^7 photons per second and a beam divergence of 0.03°. The incident beam had a diameter of 0.5 mm, which was sufficiently small to ensure that the incident beam footprint was never larger than the dimensions of the sample, but sufficiently large to gain ensemble information about the faceting.

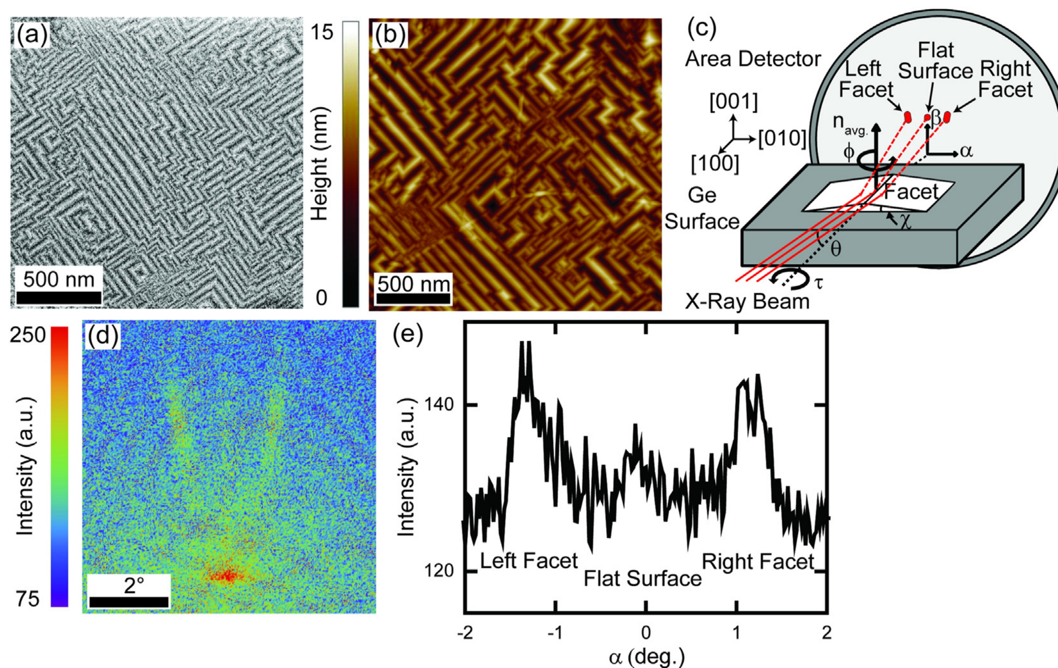

Fig. 1. (a) SEM and (b) AFM images of faceted Ge (001)/graphene. (c) Schematic of the geometry of the x-ray experiment. Reflected x-rays form three distinct spots: one from the right facet, one from the left facet, and one from the flat surface. The geometry of the problem is defined by three angles. The x-ray incident angle relative to the average surface is given by θ. The total angle of the reflecting plane is τ and ϕ is the angle of azimuthal sample rotation around the average surface normal. The angle χ defines the angle of the facet with respect to the average surface. The angular location of the reflected x-ray beams is given by the angles α and β. (d) X-ray scattering pattern acquired with an incident angle of 4°, from the Ge/graphene sample grown at 910 °C. The center streak is the x-ray reflection from the portion of the surface aligned with the average surface. The left and right streaks arise from reflections from the left and right facets. (e) Intensity profile taken horizontally across the image in (d).

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