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The impact of substrate selection for the controlled growth of graphene by molecular beam epitaxy



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ABSTRACT

We examine how substrate selection impacts the resulting film properties in graphene growth by molecular beam epitaxy (MBE). Graphene growth on metallic as well as dielectric templates was investigated. We find that MBE offers control over the number of atomic graphene layers regardless of the substrate used. High structural quality could be achieved for graphene prepared on Ni (111) films which were epitaxially grown on MgO (111). For growth either on Al₂O₃ (0001) or on (6√3 × 6√3)R30°-reconstructed SiC (0001) surfaces, graphene with a higher density of defects is obtained. Interestingly, despite their defective nature, the layers possess a well defined epitaxial relation to the underlying substrate. These results demonstrate the feasibility of MBE as a technique for realizing the scalable synthesis of this two-dimensional crystal on a variety of substrates.

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1. Introduction

Graphene, a single layer of carbon atoms arranged in a two-dimensional hexagonal lattice, is widely regarded as a revolutionary material, due primarily to its electronic properties [1–3]. The high charge carrier mobility and the ambipolar field effect measured in graphene are particularly appealing for electronic device applications [4]. Furthermore, it is known that ordered stacks of multiple graphene layers (e.g. bi- or trilayer graphene) also possess intriguing features, such as an electric field and stacking-order-dependent band structure [5–7]. These phenomena are not observed in monolayer graphene and open yet more exciting possibilities, such as the realization of devices with a gate-tunable band gap [7,8].

Hence, in terms of synthesis, a consensus has formed that the growth of high-quality, large-scale graphene films with precise control over the number of atomic layers is critical since it will enable applications where not only mono-, but also few-layer thick films will be required [9]. Although techniques such as SiC surface graphitization [10–12] and chemical vapor deposition (CVD) on Cu [13,14] have proved to be suitable for large-area synthesis, both have inherent drawbacks. The former method is restricted to a single substrate material (which happens currently to be costly). In addition, the controlled growth of a specific

number of graphene layers on SiC with complete thickness homogeneity remains challenging. CVD on Cu produces continuous graphene films which are exclusively one monolayer thick, since the precursor molecules are efficiently cracked only at the original, exposed metal surface. Similar to graphene growth on SiC, despite intensive ongoing research, the controlled formation of uniform few-layer graphene on Cu remains to be demonstrated. In this context, molecular beam epitaxy (MBE) appears to be a promising alternative. MBE is one of the most prominent techniques for the production of high-quality, single-crystal semiconductor films and multilayer heterostructures [15]. MBE typically does not involve catalytic surface processes, and thus holds promise for the growth of one to ~few graphene layers on a wider variety of substrates, including insulators and semiconductors. Exact deposition rates and sub-monolayer thickness control are additional significant advantages offered by MBE which will be required to achieve well-controlled, layer-by-layer graphene growth.

Although it is a relatively new topic of study within the MBE community, there have been several attempts to prepare graphene by employing this method. Previously examined templates include Si [16,17], SiO₂ [18], SiC [19], Al₂O₃ [17,20–22], Ni [23,24], and mica [18,25]. The various substrates and growth conditions used during synthesis resulted in carbon materials with different structural quality and morphology, ranging from highly disordered sp²-bonded carbon [16–18] or nanocrystalline (defective) graphene layers [17,20–22], to state-of-the-art quality graphene (either continuous layers [24] or isolated islands [25]). In spite of the apparent discrepancy between results, the collection of existing studies nevertheless already point to the fact that MBE is indeed a

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promising technique for achieving the controlled growth of graphene over large areas. In addition, from a fundamental point of view, MBE is an ideal tool for generating a detailed understanding of nucleation and growth mechanisms due to its compatibility with in situ characterization. This is especially important as graphene growth has developed into a rich research field in its own right. It has already been shown to differ from conventional thin-film epitaxy in significant ways, following mechanisms such as van der Waals epitaxy and growth from below [18,21,24,25]. In this context, it is important to mention other studies regarding graphene growth in UHV (by both physical vapor deposition [PVD] and CVD) which have closely replicated MBE growth conditions. In particular, surface scientists have carefully examined graphene formation on metals such as Ru, Ir, Cu and Au, often using powerful in situ characterization techniques such as low-energy electron microscopy (LEEM). These studies have revealed a rich, complex array of growth phenomena [26–31]. This body of literature – of which the cited references are only a few examples – may not be MBE growth in the strictest terms, but does serve to illustrate the utility of a well-controlled, the UHV growth method in the study of graphene synthesis.

In this contribution we report research aimed at the controlled preparation of graphene layers by MBE. We focus specifically on how the choice of substrate impacts the properties of the resulting graphene film by comparing and contrasting results obtained for growth on three very different surfaces as illustrative examples: Ni (111) films which were epitaxially grown on MgO (111), Al₂O₃ (0001), and SiC (0001) (offering a (6√3 × 6√3)R30° C-rich surface reconstruction). These results demonstrate the potential of MBE for the realization of the controlled epitaxial growth of graphene films (mono- to few-layer thick) with substrate flexibility.

2. Experimental

Graphene growth was performed in a dedicated MBE system with a base pressure of 1×10^{-10} mbar. The system is equipped with a solid carbon source composed of a resistively heated highly oriented pyrolytic graphite (HOPG) filament that operates nominally

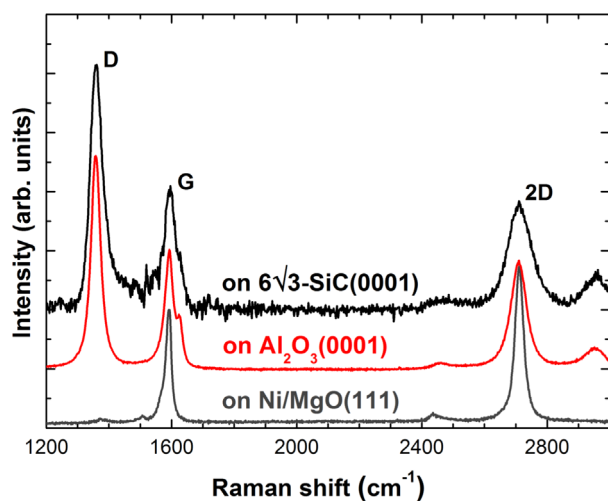


Fig. 1. Raman spectra of MBE grown graphene films on Ni/MgO (111) (gray), Al₂O₃ (0001) (red), and reconstructed 6√3-SiC (0001) substrates (black). The film grown on Ni/MgO (111) was deposited at a substrate temperature of 765 °C over 120 min (average thickness of 2 MLs) while those on Al₂O₃ and SiC were grown at 900 °C and deposition times of 240 min (average thickness of 1.5 MLs). The intensity is normalized with respect to the G peak, the spectra are offset for visibility, and the substrate related background signal is subtracted from the spectrum recorded on SiC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between 2200 and 2400 °C. In this temperature range the carbon flux is $\sim 6 \times 10^{12}$ atoms/cm² s. All substrates [the Ni/MgO (111) and SiC (0001) were sized 1 cm², and Al₂O₃ (0001) were full two-inch wafers] were degassed in a preparation chamber at 350 °C for 30 min before transfer to the growth chamber. Note that all substrates employed a 1 μm thick Ti film (deposited *ex situ* by RF-sputtering) on the backside to allow non-contact radiative heating. In the case of Ni/MgO (111), 150 nm thick epitaxial Ni (111) films were grown on MgO (111) in the same MBE cluster prior to carbon deposition. The 2.490 Å in-plane lattice parameter of the (111) Ni surface closely matches that of graphene. More details about the synthesis of the Ni (111) films can be found elsewhere [24]. For the SiC (0001) substrates, the surface preparation which allows for the creation of a (6√3 × 6√3)R30° reconstruction (referred to as 6√3, for simplicity) is performed *ex situ* at high temperatures (~ 1450 °C) in a RF-furnace prior to introducing the sample to the MBE cluster. The thermal annealing procedures utilized for this can be found in Ref. [32]. The MBE growth of graphene was performed using different growth temperatures and times. The temperature chosen for graphene growth on Ni/MgO (111) was 765 °C, with deposition time ranging from 40 to 200 min. For Al₂O₃ (0001) and 6√3-SiC (0001) growth temperatures ranging from 900 to 1000 °C were employed, with a growth time of 240 min. The structural properties of the grown films were investigated by Raman spectroscopy. The spectra shown in the next section, which were acquired with a spatial resolution of 1 μm and excitation wavelength of 482 nm, are representative of large-area growth by MBE. Analyses of different surface regions yielded similar results. In addition, scanning electron microscopy (SEM) and grazing-incidence X-ray diffraction (GID) were used to investigate the surface morphology and structure of the samples, respectively.

3. Results and discussions

Raman spectroscopy, which is a commonly accepted proxy for the crystalline quality of graphene [33,34], was used to examine the resulting films. Representative spectra are shown in Fig. 1 for graphene grown on each substrate examined here, with each displaying the characteristic peaks of *sp*²-bonded carbon. The appearance of well-defined and intense G and 2D peaks is clear evidence for the formation of graphene. In the case of graphene grown on Ni/MgO (111) (gray spectrum), the negligible intensity of the D peak indicates that extremely few structural defects, such as point vacancies or rotational grain boundaries, are present in the film. This is corroborated by the narrow widths (full widths at half maxima–FWHM) of the G and 2D peaks, $w_G = 17$ cm⁻¹ and $w_{2D} = 32$ cm⁻¹, which show the presence of a well-ordered crystal structure with a degree of perfection similar to that observed in exfoliated graphene flakes [33,34] and CVD-prepared layers [14]. The high crystalline quality of the graphene is consistent with its relatively low nucleation density on Ni/MgO (111) substrates (Fig. 4a), which is facilitated by significant carbon adatom diffusion on the metallic surface. This leads to a correspondingly low line-density of grain boundaries, regardless of the crystallographic orientation of the individual domains.

Raman spectra from graphene grown on Al₂O₃ (Fig. 1, red) and 6√3-SiC (black) both reveal similar features. The intense defect-related D peaks but well-defined and symmetric G and 2D peaks in spectra from films grown on both dielectric substrates are characteristic of defective graphene [34,35]. The peak intensity ratios I_D/I_G are comparable for both samples (1.9 for Al₂O₃ and 2.1 for 6√3-SiC). However, the FWHM of the peaks are considerably lower in case for growth on Al₂O₃ ($w_D = 34$ cm⁻¹, $w_G = 32$ cm⁻¹, and $w_{2D} = 56$ cm⁻¹) when compared with graphene synthesized on the 6√3-SiC ($w_D = 43$ cm⁻¹, $w_G = 42$ cm⁻¹, and $w_{2D} = 75$ cm⁻¹). Empirical

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