Raman spectroscopy and tunneling microscopy on epitaxially grown graphene nanoribbons

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Motivation:

Graphene nanoribbons (GNR) are an essential building block of future graphene based electronic devices due to their unique electronic properties, such as a band gap scaling with the width of the ribbon in armchair type ribbons [1,2] or the presence of topologically protected edge states in zig-zag GNR[3]. Unfortunately, GNR produced by standard lithography methods were shown to suffer severely from the initial patterning process revealing rough and disordered edges [4,5].

The growth of graphene and graphene nanosturctures by means of the so-called sublimation epitaxy on silicon carbide (SiC) samples turns out to be a promising alternative. As shown recently by our group, sidewall GNR grown on prestucured SiC-nanofacets exhibit room-temperature ballistic transport properties with electronic mean free paths up to 15 µm [6]. However, roughness besides that of the mesa structure itself is highly detrimental. Despite the intensive characterization of sidewall GNR [6,7] the physical origin of the exceptional transport properties is still unknown.
In this joint project, we intended to gain a deeper insight into the growth process of sidewall epitaxial graphene nanoribbons. Besides AFM and TEM, scanning tunneling microscopy (STM/STS) as well as Raman spectroscopy were used to characterize the GNR structures. Thereby, we addressed three main questions regarding the potential growth of multilayers, doping, and the orientation of the ribbons.

Results & Discussion:
After a predetermined thermal treatment of the SiC(0001), basically to remove residual scratched from former polishing steps, and subsequent mesa-structuring by means of optical lithography and RIE etching (for details see Ref.[8]), a final high temperature step around 1500°C for 10min. results in selevtive growth of GNR at the edges of the SiC-mesa. For the case of uniaxial mesa structures with a pitch widths of 2µm the corresponding AFM image is shown in Fig.1a. The selective growth is nicely demonstrated by electrostatic force microscopy (EFM) seen as white strips in the lower part of Fig.1a.

As mentioned above, the orientations of the edges of these GNR structures are crucial for the electronic transport properties. Figure 1b) shows an atomically resolved STM image taken in the center of a sidewall GNR. As obvious the sidewall ribbon is oriented in zig-zag direction as expected for a mesa orientation along the <-1100>-direction. Most likely also the edges should reveal this zig-zag type orientation. However, their direct imaging with atomic resolution failed most likely due to the strong local inhomogeneity with respect to the morphology and band structure.
Subsequently, tunneling spectroscopy was carried out with the same tip on the same sample area, leading to the spectra in Fig.1c). The dI/dV versus bias voltage exhibit the typical V-shape expected for graphene. Tunneling spectra recorded besides the ribbon on the mesa top (bottom) show band gaps of 1.3 eV (0.8 eV) indicating the presence of buffer layer growth and ensuring that the ribbon is electronically isolated from each other. Most importantly, the minima of the dI/dV of all spectra taken on the sidewall ribbon are precisely located at zero bias indicating charge neutrality which an important requsite for the ballistic transport behavior [8].

The method of choice for answering the question of multilayer contributions is Raman spectroscopy. A typical Raman spectrum of a sidewall GNR is shown in Fig.1d). All three visible peaks D (1382 cm^{-1}), G (1606 cm^{-1}), and 2D (2735 cm^{-1}) are characteristic for graphene. The peak positions are fully consistent with those for epitaxial monolayer graphene [9] From the ratio I(D)/I(G)=0.14 the mean distance between defects was estimated to be larger than 40 nm [10]. The 2D peak can be fitted with a single Lorentzian with a line width of 40 cm^{-1}, a clear signature for monolayer graphene [11]. The mapping of the 2D peak shown in the inset confirms agai the growth of graphene only at the mesa sidewalls.

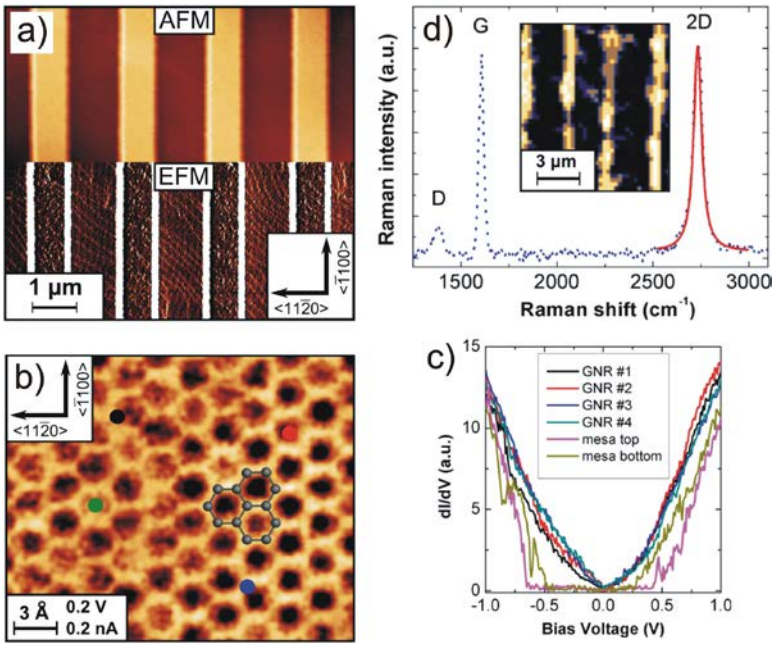

Figure 1: a) AFM (top) and EFM image (bottom) of SiC samples after mesa structuring (1µm spacing)and graphene growth at the edges. b) Atomically resolved STM image of the nanoribbon. The points mark the positions of the tunneling spectra shown in (c). (c) STS of a sidewall GNR and of the surrounding buffer layer. d) Raman spectrum of sidewall graphene nanoribbons. The inset shows a mapping of the 2D peak intensity.

To summarize we have characterized in this joint collaboration GNRs, grown selectively on the sidewalls of SiC mesa. The identification of charge neutrality, monolayer thickness as well as the zig-zag orientation is important and a prerequsiste for the ballisitic transport behavior.

Moreover, we measured in this context (not shown here) also single-channel ballistic transport by means of local 4-point probe experiments. Thereby, the mean free path of the ballistic ribbons was shown to be limited by the terrace width of the substrate. Additionally, a transition from diffusive to ballistic transport dependent on the roughness of the mesa sidewall was observed. Therefore, both the careful control the substrate roughness as well as the smoothness of the mesa sidewalls is essential for the synthesis of ballistic sidewall nanoribbons. For more details, the interested reader is referred to*: J. Baringhaus et.al., Applied Physics Letters 106, 043109 (2015)*

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