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Low-temperature synthesis of large-area graphene-based carbon films on Ni

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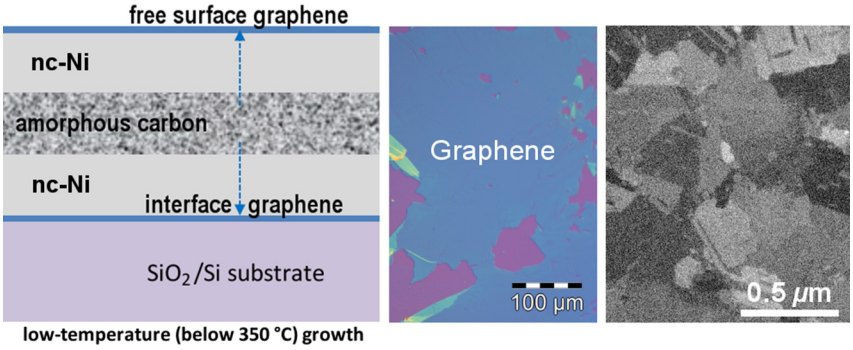
HIGHLIGHTS

- Large-area multilayer graphene film was synthesized on poly-Ni surface at low temperatures (< 350 °C);
- A Ni-C-Ni sandwiched structure was used for growth of graphene both on poly-Ni free surface and along the Ni/SiO_2 interface;
- TEM study revealed two synergistic growth mechanisms of graphene: stacking growth and crossing grain boundary growth;
- The growth kinetics of graphene was scrutinized at different temperatures and for different times;
- This work provides an attractive strategy for industrial scale manufacturing of large area graphene at low temperatures.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, large-area graphene-based carbon films were synthesized through a fast and low-temperature method. The processing route is illustrated on a free surface of Ni catalyst film by vacuum thermal processing of amorphous carbon. Key in the novel approach is that the synthesis is done at low temperatures, i.e. below 350 °C, and within a time as short as 1 min. The nucleation and growth of graphene on the free surface of nickel and along the interface between Ni film and SiO_2 substrate are investigated by using a thin film Ni-C-Ni sandwiched structure on a SiO_2/Si substrate. Raman spectroscopy demonstrates that the graphene-based carbon films consist of graphitic carbon rich of defects. HR-TEM observations reveal that the graphene-based carbon film grown on the top free surface is composed of thin multilayer graphene segments (3–6 atomic layers) and thick multilayer graphene segments (more than atomic 10 layers), covering the entire surface of Ni film over a large area. Growth parameters such as growth time, growth temperature and carbon/Ni ratio are reported in detail for a control of graphene growth kinetics. The results point at several attractive strategies for the facile synthesis of graphene-based carbon films for industrial applications.

1. Introduction

It goes without saying that graphene became an astonishing functional material in various fields of fundamental research and applications, e.g. electronics, energy conversion and storage, biological

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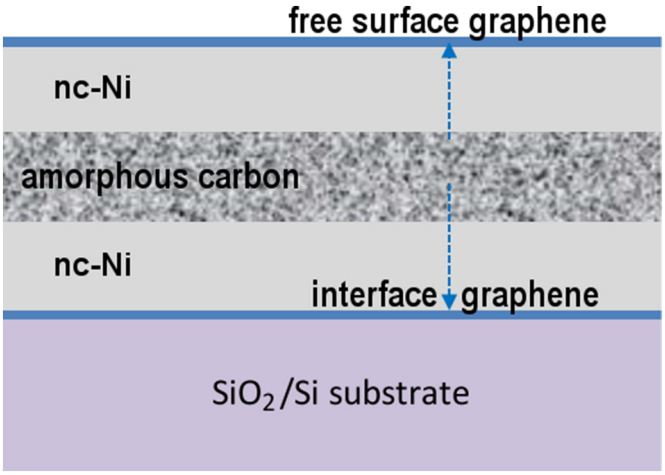

Fig. 1. Schematic illustration of the designed Ni-C-Ni sandwich film and graphene formation on the free surface of Ni film and at the interface of Ni/SiO_2 via vacuum thermal process (VTP). The thickness of nc-Ni layers was 100 nm, and the thickness of the amorphous carbon intermediate layer was varied between 10 and 100 nm.

engineering, catalysis, environment protection, water purification etc. [1–7]. The synthesis of graphene films is vital for up-scaling in industrial applications. Chemical vapor deposition (CVD) made a considerable impact in large-area and large-scale graphene production based on sacrifices of catalyst (transition metals, ceramics, etc.) [8,9]. Unfortunately, CVD growth of graphene needs high temperature, i.e. ~1000 °C [8,10], and also other thermal synthesis methods for producing graphene are executed at high temperatures [11,12]. The high processing temperature induces several critical issues, such as a limiting choice of substrates, expensive equipment, and it also requires a rather complex transfer process. Progress in exploring low temperature growth of graphene has been achieved through different strategies, for instance using liquid or solid carbon precursors, design of alloy catalysts, Sn catalyst, (microwave) plasma-enhanced CVD, and implanting carbon in metallic catalysts, etc. [13–20] and non-metallic substrates [22,23]. As a result low temperature growth of graphene has been broadly studied in many different fields, e.g. electrocatalysts, transparent conductive films (TCFs), anti-corrosion, biological coatings, etc. [14,16,18,19,22,23].

Although significant progress has been made in the field of low temperature growth of graphene by sacrificing metal catalysts, the growth mechanism and resulting microstructures are still not fully understood. The low-temperature growth mechanism of graphene cannot be simply explained by normal CVD processes. The growth mechanism of graphene on Ni by CVD has been elucidated as the rearrangement of the dissolved carbon atoms on nickel (111) from bulk nickel, driven by the different soluble capacities at different temperatures [24]. But for low temperature growth of graphene on nickel, many conditions have been altered, such as unfavorable decomposition temperature of hydrocarbon gases and the interaction between Ni and carbon, etc. Therefore the growth kinetics of graphene at lower temperatures is rather different [25,26]. Previous research concentrated on the use of amorphous carbon as feedstocks for graphene growth [27–32]. However, the graphene growth was performed at high temperatures (>650 °C). No publication has reported the conversion of amorphous carbon to graphene on Ni surfaces at such a low temperature. As far as the mechanism is concerned there are also major differences. At high temperatures, the temperature and cooling rate significantly influence the growth of graphene on Ni as carbon segregation is mainly driven by the decrease of carbon solubility in Ni during cooling [8,11,27]. But at low temperatures, the solubility is very low and is not affected. The diffusion and segregation processes of carbon differ from those at high temperatures and rely on the concentration gradients. Even in recent work reporting conversion of amorphous carbon to graphene at 250 °C by using tin as catalyst [21], only discontinuous graphene flakes were formed. In particular, Weatherup et al. reported that graphene with domain sizes of >220 μm^2 could grow on polycrystalline Ni-Au catalyst films at 450–600 °C, indicating the possibility of large-area graphene

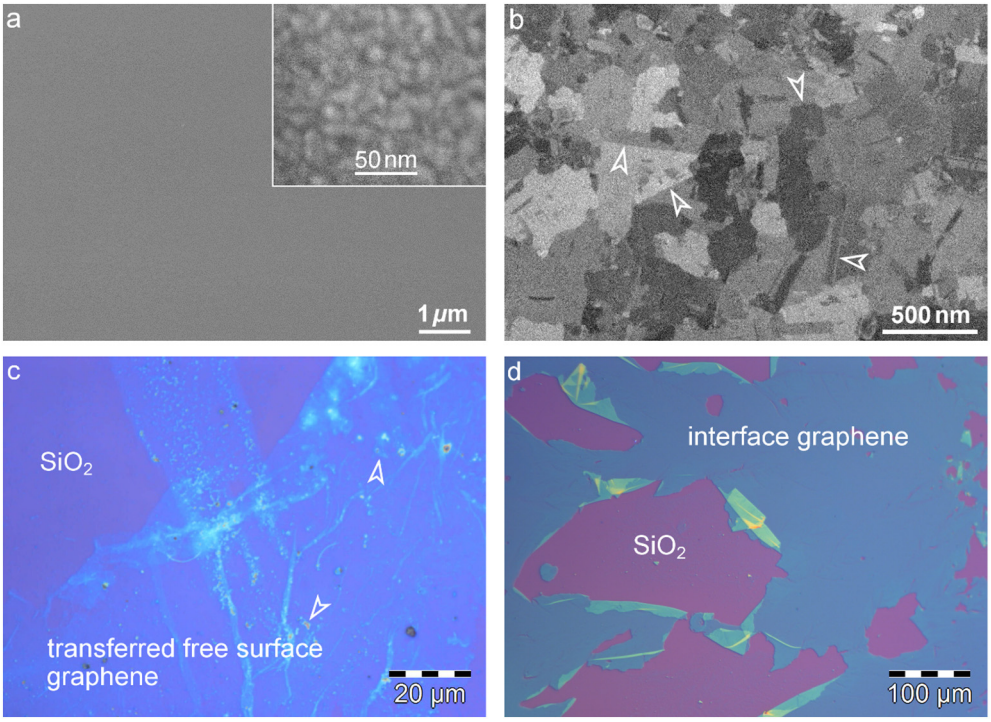

Fig. 2. SEM images showing the surface structure of Ni-C-Ni sandwich film before (a) and after (b) vacuum thermal processing at 350 °C for 12 h, with the inset of (a) at high magnification revealing a grainy surface morphology of the top Ni film before treatment, the white arrows in (b) point out the boundary of micron-sized multilayer graphene segments; Optical images of transferred free surface graphene-based carbon film from the Ni surface (c) and the remaining interface graphene-based carbon film on SiO_2 substrates after etching away Ni (d), the arrows in (c) show multilayer graphene fragments.