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Large area CVD growth of graphene

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ABSTRACT

During the past decade, graphene, a single layer of sp^2-hybridized carbon atoms, has attracted enormous interest among scientists due to its unique physical, mechanical and electrical properties. Recently developed chemical vapor deposition technique has emerged as the most popular method for the scalable production of large-area and high-quality graphene for various applications. The key objective of this article is to provide a detailed and up to date review on the synthesis of large area monolayer, bilayer and multilayer graphene on different substrates via chemical vapor deposition method. Challenges and future perspective in this field are highlighted.

1. Introduction

Graphene is an ideal one-atom-thick two-dimensional material of sp^2-bonded carbon atoms [1–3], and has been receiving significant attention owing to its exciting characteristics such as quantum Hall effect [4,5], superior thermal conductivity [6–8], and ultra-high carrier mobility [2,3], etc. The utilization of these outstanding properties of graphene has been screened for a variety of applications: such as transistors [9], sensors [10,11], actuators [12], flexible and transparent conducting films [13]. However, for practical applications, a reproducible and large-scale production of graphene is of vital importance. Graphene can be prepared by mechanical exfoliation of graphite [14], epitaxial growth on SiC surfaces [15–17], reduction of graphene oxide [18,19], and chemical vapor deposition (CVD). Among these strategies, CVD has become the most promising approach because it is inexpensive, transferrable and it has the ability to produce high quality and large-area graphene films [20,21]. CVD graphene was first reported in 2008 and 2009, using Ni and Cu as substrates [22,23], which was then followed by an explosion of research activities. To date, many problems still remain, hampering the further development of graphene in fundamental research and practical application. This review article summarizes the main techniques used for the synthesis of large area graphene by CVD methods. Recent important advances in controllable synthesis of large-area monolayer, wafer-scale single crystal, bilayer and multilayer graphene on metal and insulating substrates are presented. Finally, problems and future perspectives are discussed.

2. Mechanism of chemical vapor deposition of graphene

High temperature decomposition of various hydrocarbon sources by CVD method to produce thin, graphitic layers on transition metal surfaces and metal carbides have been studied for over 60 years [24]. The growth process involves the thermal decomposition of a hydrocarbon source on a heated substrate. Depending on the substrate, the process can be catalytically enhanced. Transition metals are the most widely used substrates in graphene synthesis. During the reaction, the metal substrate not only works as a catalyst to lower the energy barrier of the reaction, but also determines the graphene deposition mechanism. Table I lists out the solubility of carbon in various metal substrates and the corresponding growth mechanism. In the case of metals having high carbon solubility (such as Ni and Fe), the carbon will diffuse/dissolve into the heated substrate according to the solubility of carbon. As the substrate cools, the dissolved carbon will segregate to the surface to form graphene sheets [22,25,26]. This "segregation" process is depicted clearly in Fig. 1a [22]. On the other hand, for metals with low carbon solubility (such as Cu), carbon atoms will nucleate and laterally expand around the nucleus to form graphene domains with decomposition of hydrocarbon catalyzed by the substrates at high temperature. The growth process will terminate when the substrates are fully covered by the graphene layer, which is usually referred as a "self-limited surface deposition" growth mechanism (Fig. 1b) [27]. Recently, it has been observed that the self-limiting growth process could be broken on Cu and few layer graphene can be produced under special growth conditions, such as

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Table I
Carbon solubility and the growth mechanism on typical metals for CVD graphene.

Metal (bulk)	Carbon solubility at 1000 °C (at.%) [38]	Primary growth mechanism
Copper(Cu)	0.04	Surface deposition [20,23,27,39–42]/penetration [31,32]
Cobalt (Co)	3.41	Segregation [43]
Platinum (Pt)	1.76	Segregation [44–47]/surface deposition [48,49]
Nickel (Ni)	2.03	Segregation [50–55]/surface deposition [56]
Palladium (Pd)	5.98	Segregation [57,58]
Iron (Fe)	7.89	Segregation [59]
Germanium (Ge) (semi-metal)	0.00	Surface deposition [36,37]

CVD growth under atmosphere pressure [28], a very slow cooling rate [29] as well as a high methane concentrations [30].

Despite the low carbon solubility in Cu, several researchers have observed the segregation growth mechanism occurred on Cu enclosure, where carbon species penetrate from one side of the Cu foil to the other side, and then forms the second layer or multilayer graphene underneath the top first layer [31,32]. This mechanism is denoted as the "penetration" growth mode (Fig. 1c) [32], which favors the production of large scale graphene bilayer or multilayer, more details will be discussed later.

Besides the metal substrates, graphene synthesis on insulating substrate has been studied on several different substrates [33–35]. The growth mechanism of graphene on non-metal surfaces usually involves the surface adsorption, nucleation and coalescence. Without catalytic effect, multilayer graphene could be deposited on the insulating substrates. However, higher decomposition temperature is usually required on insulating substrates than on metal substrates such as Cu or Ni for graphene with high quality. Fig. 1d depicts the growth graphene on sapphire using methane under 1450 °C [34].

Semi-metal Germanium (Ge) has recently been reported as one of the promising substrates for direct synthesis of wafer-scale single-crystal monolayer graphene [36]. Different from other insulating substrates, the Ge surface is catalytic active which helps to lower the decomposition temperature of carbon precursor. Moreover, the deposition of graphene on Ge is observed as a self-limiting and surface-mediated process which is similar to the behavior of graphene synthesis on Cu [37]. In this review, Ge was categorized as a semi-metal and the relevant work was summarized with other metals in the Section 3.2.

3. CVD growth of large area monolayer graphene

The synthesis of monolayer graphene on various metal surfaces by CVD methods is comparatively mature [20,21]. Recent progress on the synthesis of large area monolayer and single crystal graphene on metals and insulating substrates are discussed in this section.

3.1. Monolayer graphene on copper substrate

The growth of graphene using copper as the catalyst substrate is the most popular method for preparing large-area, high quality monolayer graphene [20]. The growth mechanism on Cu surface is a surface adsorption process owing to the low solubility of C atoms in Cu, offering a path to grow monolayer graphene based on self-limiting process [23,39].

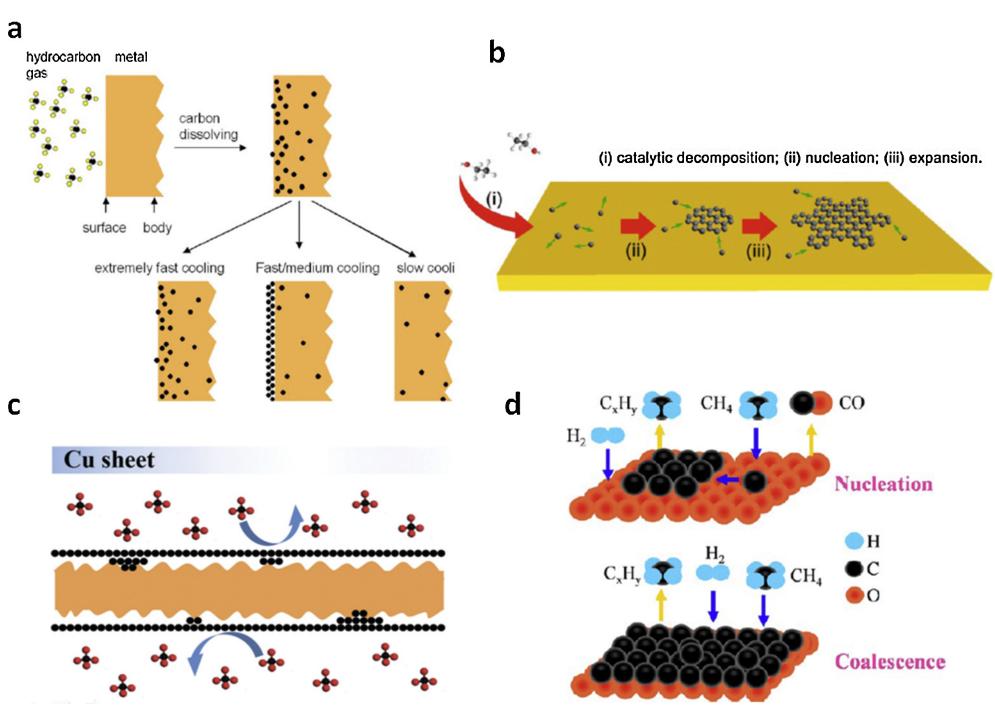

Fig. 1. Schematics of CVD graphene grown on (a) metals with high carbon solubility, (b) Cu foil, (c) Cu enclosure, and (d) sapphire.
Adapted with permission from Ref. [22,27,32,34].