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Direct synthesis of few- and multi-layer graphene films on dielectric substrates by "etching-precipitation" method

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ABSTRACT

A novel "etching-precipitation" method is proposed and developed for the direct synthesis of graphene on dielectric substrates. In this method, graphene precipitates from the Fe–C solid solution film during selective etching of Fe using Cl_2 gas. Few- and multi-layer graphene is fabricated directly on quartz glass and SiO_2/Si substrates without Fe residue at a growth temperature of 500–650 °C, which is a significantly lower temperature than used in the conventional chemical vapor deposition method. The 6- to 7-layer graphene synthesized at 650 °C shows a volume resistivity of 80–140 μΩ cm. The average number of layers can be easily controlled in a linear fashion with the initial carbon feed, which is proportional to the thickness of the starting Fe–C films. Line-patterned multi-layer graphene is also fabricated by simply pre-patterning the starting Fe–C film although its structure is somewhat different from typical graphene ribbons. "Etching-precipitation" will be a practical route to synthesize graphene with micro-patterns directly onto device substrates of arbitrary sizes.

1. Introduction

Graphene [1], which is a monolayer or few layers of sp^2 bonded carbon atoms, has been attracting much attention since Novoselov et al. revealed its unique properties in 2004 [2]. Graphene's tunable energy band structure, high carrier mobility, mechanical/chemical stability, and acceptable optical transparency can enable various applications such as transparent electrodes, transistors, and wirings in large-scale integrated circuits (LSIs) by adjusting the layer number [3–5]. Therefore, fabrication methods that provide good control over the structure and layer number of graphene have been extensively explored. Currently, chemical vapor deposition (CVD) on catalyst metals [6–20] is considered the most promising method for the synthesis of graphene because of its high scalability. Graphene films 30 inches in size were produced for transparent electrodes by CVD on Cu foils, and transparent electrodes having a sheet resistance of 30 Ω/sq. and an optical transmittance of 90% (excluding the absorption by the base film) were fabricated by transferring graphene four times to polyethylene terephthalate films [7]. For many applications, it is necessary to have graphene on dielectric substrates.

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The transfer of graphene to such substrates has been realized by complete etching of the catalyst metals by liquid etchants (e.g., $FeCl_3$ aq) [7–18] and, more recently, by the electrochemical delamination or electrolysis-based bubbling transfer method [21,22]. However, wet processes can easily cause impurities and damage to graphene, resulting in an increase in resistivity or degradation of mobility. Furthermore, it is very difficult to fabricate graphene with a micro-pattern on a patterned underlayer, such as is necessary for creating wiring in LSIs. To solve the transfer process difficulties, some groups have recently reported the synthesis of graphene between the catalyst metals and the dielectric substrates [23–27], and the synthesis of graphene by CVD without a metal catalyst [28,29]. However, the synthesis of graphene possessing an acceptable level of quality and uniformity directly on dielectric substrates is still a challenge, and a breakthrough toward obtaining good controllability over the layer number and micro-patterning is in high demand.

In this study, we propose an "etching-precipitation" method that enables the direct synthesis of metal-free graphene on dielectric substrates. Fig. 1 is a schematic comparing the etching-precipitation method with the ordinary CVD method. Two types of metal catalysts are used for CVD. In the case of carbon-insoluble metals (e.g., Cu) [6–12], carbon feedstock (e.g., CH_4) decomposes on the catalyst surface and forms graphene through a surface reaction mechanism [11] (Fig. 1a). In the case of carbon-soluble metals (e.g., Ni, Co, and Fe) [11–18], the carbon feedstock decomposes on and dissolves into the catalyst, and the carbon precipitating from the catalyst upon cooling [11] predominantly contributes to the graphene growth with some contribution from the surface reaction mechanism [30] (Fig. 1b). In case of CVD at low temperatures, these metals have lower solubility of carbon and yield graphene also via the surface reaction mechanism, as previously reported for the Ni–Au alloy catalyst at 450 °C [31]. Uniform monolayer graphene was recently realized through the surface reaction mechanism on the Ni–Au ally catalyst by CVD at 600 °C via the careful control over the surface reaction and bulk diffusion kinetics [32]. For the case of CVD at high temperatures, the carbon supersaturation that occurs because of the reduced solubility of carbon in catalyst metals during cooling drives the carbon precipitation from the metal–carbon solid solution [11]. More precisely, the driving force for the precipitation of carbon is the lower chemical potential of carbon in graphene/graphite than that in the supersaturated metal–carbon solid solution. This gives birth to the new idea of driving the precipitation of carbon not by decreasing the solubility of carbon, but instead by increasing the carbon concentration in the solid solution. We propose the etching-precipitation method for graphene synthesis in which the solute carbon is supersaturated by removing the solvent metal from the "hot metal–carbon solid solution" through dry-etching (Fig. 1c). We can choose the metal from the carbon soluble metals such as Fe, Co, and Ni, and Fe having a high carbon solubility (up to 25 at% in a form of Fe_3C carbide) is selected in this work to achieve rather thick graphene for possible application to wiring in LSIs. The Fe–C mixture film is deposited on either quartz glass or an SiO_2/Si substrate and heated to 400–700 °C, whereupon the Fe is gradually etched away by Cl_2 gas to yield graphene directly on the SiO_2/Si without metal residue. Few-layer graphene and multi-layer graphene, which are defined as graphene having 2–5 and 2–10 layers, respectively [1], can be obtained with a moderate process temperature of 500–650 °C because the graphene growth proceeds at a constant temperature, thereby keeping the carbon mobile. Furthermore, control over the number of graphene layers as well as patterned growth, which are important base technologies for wiring in LSIs, are realized by tailoring the structure of the initial Fe–C mixture films.

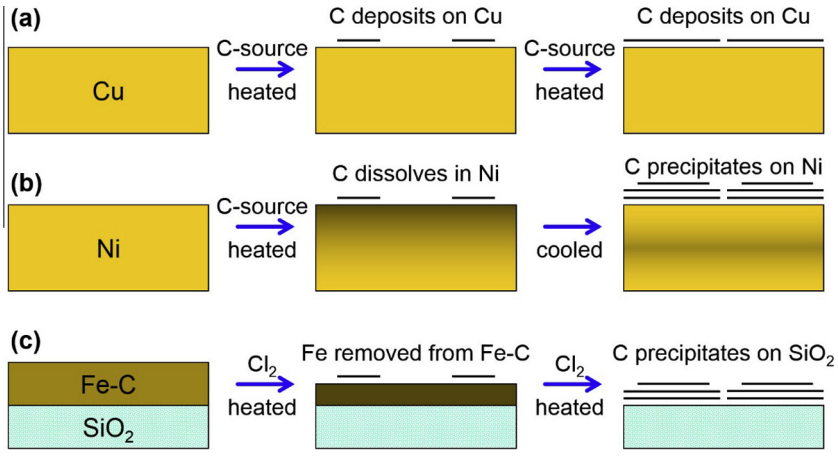

Fig. 1 – Schematic comparing the CVD and "etching-precipitation" processes. (a) In a CVD process using a carbon-insoluble metal catalyst such as Cu, the graphene growth proceeds through the surface reaction [11]. (b) In a CVD process using a carbon-soluble metal catalyst such as Ni, the graphene growth proceeds through carbon supersaturation and precipitation from the Ni-C solid solution upon cooling [11], as well as through the surface reaction [30–32]. (c) In the etching-precipitation of the metal-C mixed film (e.g., metal = Fe), the graphene growth proceeds through carbon supersaturation and precipitation by removing solid-solvent Fe, resulting in Fe-free graphene directly on the substrates. (A color version of this figure can be viewed online.)