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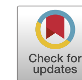
Research paper

Formation process of graphite film on Ni substrate with improved thickness uniformity through precipitation control



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ABSTRACT

Large-scale graphitic thin film with high thickness uniformity needs to be developed for industrial applications. Graphitic films with thicknesses ranging from 3 to 20 nm have rarely been reported, and achieving the thickness uniformity in that range is a challenging task. In this study, a process for growing 20 nm-thick graphite films on Ni with improved thickness uniformity is demonstrated and compared with the conventional growth process. In the film grown by the process, the surface roughness and coverage were improved and no wrinkles were observed. Observations of the film structure reveal the reasons for the improvements and growth mechanisms.

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1. Introduction

While graphene and graphite have the same chemical bonding, their physical properties radically differ, due to their different physical dimensions such as thickness [1]. Studies have been conducted to discover the thickness criteria indicating the dramatic changes in optical [2,3], thermal [4,5], mechanical [6–8], and electrical properties [9,10]. While these previous reports provide important information on the optimized graphene or graphite film to each application, they are limited to their small size or impractical computer simulation results [1–10]. The preparation of large-scale graphene or graphite thin film with high thickness uniformity needs to be performed for industrial applications.

One of the industrial applications of the large-scale graphitic thin film is extreme ultraviolet lithography (EUVL) pellicle.[11] To satisfy the industrial requirement of EUVL pellicle, the free-standing graphitic film should have the thickness less than 20 nm for above 90% of EUV transmission.[12] Additionally, the film thickness should be extremely uniform because only 2 nm of thickness difference largely changes the EUV dosage onto the wafer. In our previous research, the thickness of the graphite film was easily controlled from 78 to 18 nm by the change of reaction temperature. However, it was challenging to synthesize graphitic film which has excellent thickness uniformity with the thickness less than 20 nm.[11]

The study of the graphite film growth of the thickness less than 20 nm has rarely been conducted. Graphene film synthesis has been demonstrated on transition metal substrates, such as Cu and Ni, using chemical vapor deposition (CVD) method. In the case of Cu, it is difficult to stack the additional graphene layers onto the first-grown graphene by CVD because the surface of the first-grown graphene layer is chemically stable, and the Cu surface has weak capability of decomposing hydrocarbon and supplying sufficient C atoms onto the catalyst surface is limited [13,14]. A higher pressure or significantly longer reaction time are needed to increase the film thickness; the process efficiency of the film is therefore limited [15,16]. The maximum thickness of graphene film on a Cu substrate is 3 nm [16]. As another approach, graphite film precipitation from Ni substrate has been demonstrated. The graphite growth process includes a longer carbon dissolution step (isothermal reaction step) than that of the conventional graphene growth, and is followed by a precipitation step (cooling step) [11,16,17]. In this case, securing the film thickness uniformity is challenging because the precipitation begins immediately after the carbon dissolution step and continues across a large temperature range (normally from 900 °C to 430 °C [18,19]); the process thus cannot control the graphite nucleation and growth which occurs over the entire catalyst surface. The thickness uniformity problem worsens with the decrease of the film thickness [11]. The same problem has been observed on Cu-Ni alloy [20,21].

In this research, we propose a process for the growth of 20 nm graphite film with improved thickness uniformity by controlling the carbon precipitation process on a Ni substrate. The process consists of a fast cooling step and a separated precipitation step.

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The fast cooling step, which is conducted immediately after the isothermal carbon dissolution process, prevents graphite precipitation due to the sufficient cooling rate and H_2 ambient. The separated precipitation step, where C-Ni solid solution is annealed at the optimized temperature, is conducted after the fast cooling step, whereby graphite film is formed onto the surface of the Ni. While the new process is fundamentally the same as the conventional film growth process which exploits the differences in solubility between the two different temperatures, the precipitation control in the process significantly differs to that in the conventional process. In the new process, the carbon-supersaturated solid solution is formed by the suppression of precipitation and the optimized precipitation condition is used to form the film with improved thickness uniformity.

We expect that the suppression of uncontrolled precipitation and the optimization of precipitation will be applicable to various film materials include EUVL pellicle and improve thickness uniformity of the various films obtained from precipitation process.

2. Materials and methods

A 25 μm-thick Ni foil with 99% purity (Alfa Aesar) was used as the catalyst substrate. The substrate was sonicated in acetone, methanol, and deionized water for 30 min and blown by nitrogen. A cold wall reactor with halogen lamps and a quartz chamber was used for the growth process. A schematic of the process is depicted in Fig. 1a. The process was composed of the following steps: (i) pre-annealing at 910 °C for 3 min with a H_2 atmosphere, (ii) carbon dissolution at 910 °C for 87 min with reaction gases ($H_2 : CH_4 = 5:1$, 0.38 Torr), and (iii) cooling (conventional cooling: blue line in Fig. 1a, or fast cooling: red line in Fig. 1a). Conventional cooling was conducted by switching off the heater, and the same gas condition was maintained as that of the growth process. During the fast cooling, additional Ar flow (2000 sccm, ~7 Torr) was supplied. After the conventional cooling, the graphite film was grown on the Ni substrate. However, no graphite was found on the Ni substrate after the fast cooling [22]. Additional thermal treatment was performed as a separated precipitation after the fast cooling. In the separated precipitation step, Ni was heated up to the specified temperature for 84 s in the H_2 atmosphere. After reaching the temperature, the heater was switched off again and cooled down to room temperature (RT) without supplying additional Ar flow. The graphite film was separated from the Ni substrate without any supporting layer using 10 wt% ceric ammonium nitrate aqueous solution. After rinsing with diluted hydrochloric acid and deionized water, the film was transferred onto a SiO_2 (300 nm)/Si wafer for optical microscopy, Raman spectroscopy (532 nm), and atomic force microscopy (AFM) analysis. To characterize the microstructure of the graphite film, transmission electron microscopy (TEM) images and selected area electron diffraction patterns of the free-standing film were obtained.

3. Results and discussion

Fig. 1a shows the film formation process by fast cooling step and separated precipitation step (red line, 1 → 3 → 5 → RT) compared to the conventional process (blue line, 1 → RT). Carbon atoms were dissolved in Ni during the carbon dissolution step. During the conventional process, the gas condition was kept the same as that during the carbon dissolution step and the initial cooling rate was 9 °C/s (average cooling rate of initial 10 s), and the instantaneous cooling rate was not constant during the process (the elapsed time from 910 °C to 500 °C was 158 s). After cooling, a graphite film was formed on the Ni surface and the photo image and microscopic image are shown in Fig. 1b and d, respectively. As shown in Fig. 1d, some regions are not covered with graphite (blue arrows) shown as a bright color. The film also shows a

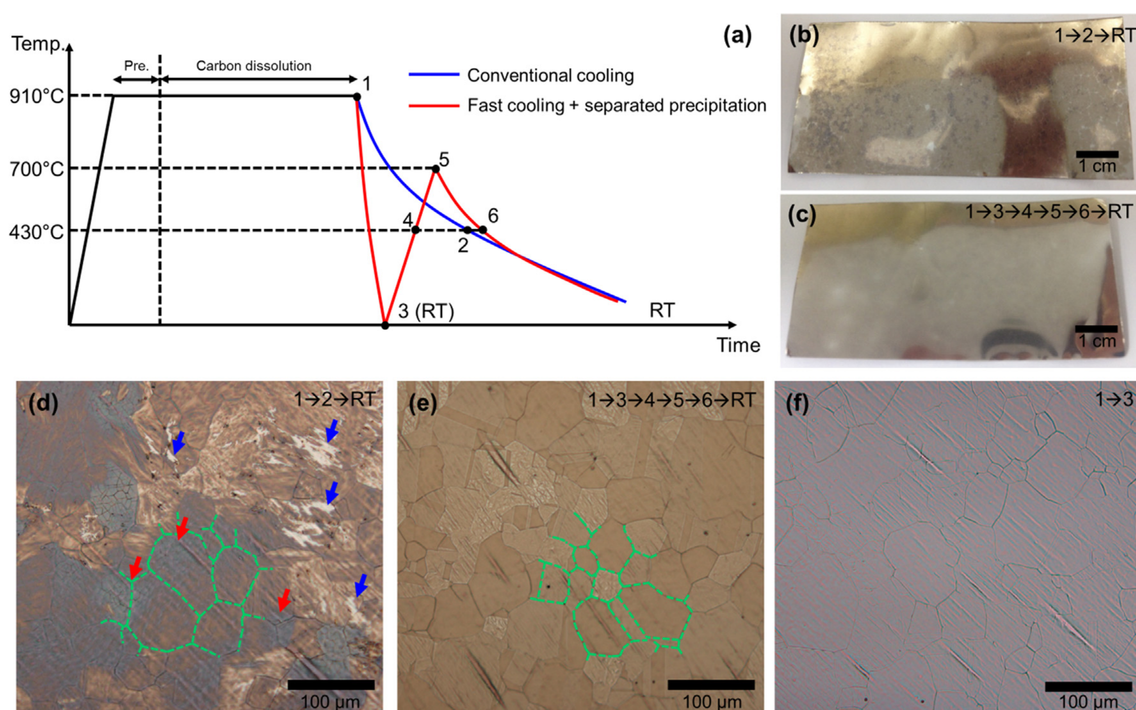

Fig. 1. (a) Schematics of graphite film growth process using fast cooling and separated precipitation (red) compared to conventional cooling (blue). (b) Photo image of the as-grown graphite/Ni after conventional cooling. (c) Photo image of the graphite/Ni after fast cooling and separated precipitation. (d) Microscopic image of (b). Blue arrows: no graphite regions. Red arrows: thick graphite regions. Dotted green lines: Ni grain boundary. (e) Microscopic image of (c). (f) Microscopic image of the Ni surface after fast cooling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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