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Full Length Article

Study on the formation of graphene by ion implantation on Cu, Ni and CuNi alloy

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ABSTRACT

This study identifies the details for direct synthesis of graphene by carbon ion implantation on Cu, Ni and CuNi alloy. Firstly, diffusion and concentration of carbon atoms in Cu and Ni are estimated separately. The concentrations of carbon atoms near the surfaces of Cu and Ni after carbon ion implantation and subsequent thermal annealing were correlated with the number of atoms and with the coverage or thickness of graphene. Systematic experiments showed that the Cu has higher carbon diffusivity and graphene coverage than Ni but higher temperatures and longer annealing times are required to synthesize graphene, similar to those in chemical vapor deposition method. The CuNi system shows better graphene coverage and quality than that on a single metal catalyst even after a short annealing time, as it has larger carbon diffusivity and lower carbon solubility than Ni and shows lower activation energy than Cu.

1. Introduction

It is well known that the properties of graphene are appropriate for various electrical and optical device applications [1–6]. Although large-area monolayer graphene of high quality can be synthesized by chemical vapor deposition (CVD) [7–11], some undesirable processes, such as coating and removing of the supporting layer based on the polymer and manual transfer of graphene onto substrates, are necessary. These undesirable processes affect the properties of graphene by generating polymer residues, wrinkles, and tears [12–14]. From the viewpoint of industrialization, it is essential that high-quality large-area graphene layers should be directly grown on the desired substrates. If general semiconductor processing, for example ion implantation and thermal annealing, can be used to grow graphene, it would be advantageous for reducing the cost of production as well as damage by transfer onto substrates.

Ion implantation is not only one of the most common processes for fabrication of various semiconductor devices, but also a highly developed process for controlling the amount and projection depth of irradiated ions. Owing to the superior advantages of the implantation technique, recently, a few results of graphene synthesized by carbon ion implantation into Cu or Ni have been reported [15–19], where Cu or Ni was used as metal catalyst. The injected carbon ions become atoms inside the metal catalyst. Cu and Ni are the most common metals used to grow graphene by CVD or by ion implantation. Many physical properties of these metals are comparable. For example, they have the same crystal structure (FCC), similar density (8.90 g/cm^3 for Ni and 8.96 g/cm^3 for Cu), and similar atomic radii (149 pm for Ni and 145 pm for Cu) [20]. However, both metals have different carbon solubility and show different growth mechanisms. It is known that Ni has high carbon solubility, and therefore, carbon atoms diffuse into Ni and then precipitate onto the Ni surface with decreasing temperature [21–23]. On the other hand, carbon atoms are only adsorbed on the surface of Cu owing to the extremely low solubility of carbon in Cu. Monolayer graphene can be produced on the Cu surface through the self-limiting effect, and therefore, the synthesis of multilayer graphene is restricted [7,23]. The introduction of carbon into the metal by ion implantation is a non-equilibrium process [24,25], which means that the number of carbon atoms introduced by ion implantation can exceed the solid-solubility limit of the metal. Most literatures that used ion implantation for growing graphene have reported that implanted carbon atoms were precipitated on the metal surface because of their low carbon solid-solubility, which helps control the number of layers [17–19]. In our previous research, graphene was formed not only on the top surface of Ni but also at the Ni-SiO_2 interface after ion implantation and heat

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treatment [26]. Therefore, the projected carbon atoms diffused inside the metal and then precipitated on the top and bottom surfaces of the metal. In this study, we calculated the concentration of carbon near the top single metal surfaces at various temperatures and times and investigated the uniformity and coverage of graphene synthesized on Cu or Ni after carbon ion implantation and heat treatment. Further, we attempted to enhance the growth of graphene using a CuNi alloy instead of a single metal.

2. Experimental methods

2.1. Sample preparation

Ni and Cu of 200 nm thick were deposited onto 4-in. SiO_2/Si (300 nm, 500 μm layer thickness) wafers using an electron-beam evaporator (UEE, ULTECH). They were implanted with a dose of 3.8×10^{15} carbon ions/cm^2 corresponding to the atomic density of a monolayer graphene film at an energy of 20 keV.

A Cu/Ni bilayer film (150/300 nm) was deposited on a 4-in. SiO_2/Si wafer using an electron-beam evaporator. Carbon ions at an energy of 190 keV and a fluence of 3.8×10^{15} ions/cm^2 were implanted onto this CuNi bilayer film sample.

The projected ranges of the accelerated carbon ions were calculated using the stopping and range of ions in matter (SRIM) Monte Carlo simulation software. The irradiated samples were annealed in a horizontal tube furnace (TF55035A, Lindberg/Blue M) at various annealing conditions (annealing time and temperature) in an Ar flow of 200 sccm. The furnace was cooled rapidly at a rate of 15 °C/s. Finally, graphene was grown on the metal film.

2.2. Optical characterizations

The synthesized graphene was characterized using an optical microscope (BX51RF, Olympus) and Raman spectroscopy, which was carried out in a back-scattering geometry using a 532 nm emission of a diode-pumped solid-state laser (Invia, Renishaw) at room temperature with a 2 μm beam size at the surface of the sample. The graphene/metal/SiO_2/silicon substrate was cut using a focused-ion beam technique (Quanta 3D 200, FEI) to prepare the specimen for transmission electron microscopy (TEM). The thickness and quality of graphene layers were estimated using TEM (Tecnai F30 G2ST, FEI).

3. Results and discussion

In a previous study, we synthesized graphene on Ni after carbon ion implantation and thermal treatment at 900 °C for 30 min [26]. Therefore, we used this temperature and time as standard conditions and then changed the growth temperature and time. First, the concentration of carbon atoms near single metal surfaces was estimated at each time and temperature because we considered that carbon atoms should arrive near the surface before precipitation. It was assumed that all irradiated carbon atoms arrived at a specific projection depth and diffused following Fick's second law that is

$$C(x,t) = \frac{C_i}{2\sqrt{\pi Dt}}\left[\exp\left[-\left(\frac{x^2}{4Dt}\right)\right]\right]$$

where C_i is the concentration of carbon at the projection depth of implantation, x is distance from the projection depth of carbon ions, D is the diffusivity, and t is the time for diffusion. The diffusion coefficients of carbon in Cu at 600 °C and 900 °C are 1.7×10^{-12} and 3.8×10^{-11} m^2/s, respectively [27–29]. The penetration depth of carbon ion with 20 keV kinetic energy into 200 nm thick Cu was 249 Å from the target surface, numerically calculated using the SRIM software. In the case of Ni, the diffusion coefficients of carbon atoms at 600 °C and 900 °C were 2.22×10^{-14} and 8.34×10^{-12} m^2/s, respectively [30]. The penetration depth of 20 keV carbon ions into 200 nm thick Ni was calculated to be 237 Å from the target surface.

Fig. 1 shows the calculated carbon concentration in 200 nm thick Cu and Ni layers. The estimated concentrations of carbon atoms at the Cu surface at 600 °C and 900 °C after 30 min were approximately 4.8×10^{11} cm^{-3} and 5.2×10^{10} cm^{-3}, respectively. Under the same conditions, the concentrations of diffused carbon at the Ni surface were almost 0 and 2.05×10^{11} cm^{-3}, respectively. The reason for the lower carbon concentration at higher temperatures on Cu is the enhanced diffusion toward the interface between SiO_2/Si and Cu. According to this estimation, graphene does not cover the entire Cu surface at 900 °C, even if it is assumed that all carbon atoms at the surface are converted to graphene, because of the lower diffused concentration than at 600 °C. As Ni has a lower diffusivity at low temperatures, it is difficult to form graphene on the surface. Some more simulation results are shown in the supplementary material (Figs. S1–S6).

The experimental results show some differences with the estimation. First, surface conditions of the metal catalysts were compared after implantation and heat treatment. Optical microscopy (OM) images show a different surface status of Cu and Ni before and after the standard treatment condition as shown in Fig. 2(a)–(c). The metal surfaces had dark stains although their size and distribution were different. As it is difficult to ensure the growth of graphene, Raman spectra were collected at a few points on each metal surface. The spectra on Cu were observed at randomly chosen locations and those on Ni were measured on the dark-gray spots (Fig. 2(c)). It was confirmed that a few layers of graphene were grown without defects on Ni, which can be inferred from the absence of a D band (~1350 cm^{-1}), whereas graphene on Cu showed a relatively large D band. However, the relatively bright locations on Ni showed neither a G (~1580 cm^{-1}) nor 2D (~2680 cm^{-1}) bands.

Fig. 3(a) and (b) indicates the effect of growth temperature at a fixed growth time (30 min) based on Raman spectra. The 2D band of multilayer graphene clearly appears and the D band reduces with 900 °C treatment on both metals, which means that the carbon atoms form a symmetric structure by sp^2 covalent bonding at this temperature. We consider that more carbon atoms added during metal deposition and thermal annealing are sources for multilayer graphene because carbon is inevitably contained, even though the theoretical dose amount for synthesis of monolayer graphene is injected [31]. It is apparent that the nucleation of amorphous carbon occurs even at 600 °C on Ni. On the other hand, the absence of any carbon-related Raman peaks on the Cu surface means that more energy is required to form bonded carbon clusters. The growth times of graphene at a fixed temperature (900 °C) were also compared as shown in Fig. 3(c) and (d). Sharp and clear G and 2D bands of graphene grown on Ni were observed at 5, 10, and 30 min of growth time, whereas relatively high G and 2D bands on Cu were observed only at 30 min. As the Raman spectra above only show the results of a few points (dark spots) on the metal surface, annealed samples at 900 °C for 30 min were investigated by Raman mapping of a 10×10 μm^2 surface to obtain more information on the coverage. In Fig. 4, the Raman results indicate that graphene synthesized on Cu covers metal surface more widely (approximately 71%) than that on Ni (17%). These coverages were estimated using ImageJ software based on the G band in the Raman spectra without consideration of the number of graphene layers.

It is reasonable that graphene does not cover the entire Cu surface according to the numerical estimation. However, the poor coverage of graphene on Ni is difficult to understand because the calculated concentration of carbon near the Ni surface was higher than that on the Cu surface. Therefore, we conclude that the dom-