Low-Temperature (400 °C) Synthesis of Multilayer Graphene by Metal-Assisted Sputtering Deposition

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ABSTRACT: Low-temperature synthesis of multilayer graphene (MLG) is essential for combining advanced electronic devices with carbon materials. We investigated the vapor-phase synthesis of MLG by sputtering deposition of C atoms on metal-coated insulators. Ni, Co, and Fe catalysts, which have high C solid solubility, enabled us to form MLG at 400 °C. The domain size and surface coverage of MLG were determined by the supplied amount of C atoms and the thickness of the metal layer associated with the solid solution amount of C. An average domain size of 2.5 μm and surface coverage of approximately 50% were obtained for a 1 μm thick Ni layer. Transmission electron microscopy demonstrated the high crystalline quality of the MLG layer despite the low processing temperature. Therefore, this simple sputtering technique has great potential for integrating graphene-based devices on various platforms.

INTRODUCTION

Multilayer graphene (MLG) is expected to be applied to low-resistance wiring, heat spreaders, and anodes for lithium-ion batteries because of its high electrical/thermal conductivities, current-carrying capacity, and specific capacity. To make use of these features, it is essential to incorporate MLG into existing devices such as large-scale integrated circuits (LSIs) or flat-panel displays. To achieve this, MLG needs to be synthesized at low temperatures to prevent damaging the underlying devices (e.g., approximately 500 °C for LSIs and a glass substrate). Low-temperature synthesis of MLG on arbitrary substrates has been achieved through vapor-phase7−14 and solid-phase crystallization15,16 processes using metal catalysts. These techniques utilize a phenomenon in which carbon atoms dissolved in the metal are precipitated as graphene. Chemical vapor deposition (CVD) was the most common method for MLG synthesis. However, because CVD requires high temperature for gas decomposition, devices such as plasma aiding are necessary to avoid raising the temperature of the sample.

Sputtering is a very simple method and is commercially superior. Metal-induced solid-phase crystallization of sputtered amorphous carbon (a-C) films,18,19 particularly via layer exchange,20−22 is useful for fabricating thick MLG films on arbitrary substrates. Conversely, there are a few reports on the vapor-phase crystallization of MLG using the sputtering method, whereas the vapor-phase crystallization is generally more advantageous for lowering the synthesis temperature than solid-phase crystallization. In this study, we explored the possibility of low-temperature vapor-phase synthesis of MLG by sputtering with metal catalysis. The metals with high carbon solid solubility allowed MLG synthesis at 400 °C.

EXPERIMENTAL SECTION

Sample Preparation. The sample preparation procedure is shown in Figure 1. (1) Fe, Co, Ni, and Cu (thickness: 50−1000 nm) were deposited on a SiO2 glass substrate at room temperature (RT). (2) The sample temperature was raised to 400 °C in 20 min and kept at 400 °C for 40 min to heat the sample uniformly. (3) C was sputtered on the metals for 1.4−27.3 min with a deposition rate of 2.2 nm/min. (4) The sample was naturally cooled to RT (for 3.5 h). All depositions were performed using radiofrequency (RF) magnetron sputtering (base pressure: 3.0 × 10−4 Pa) with Ar plasma. The RF power was set to 50 W for the metals and 100 W for C.

Material Characterization. The Raman spectroscopy was performed using a JASCO NRS-5100, whose laser wavelength was 532 nm and spot size was 1 μm. The Nomarski optical micrographs of the sample surface were obtained at a magnification of 1000X. Here, the MLG coverage was calculated using binarization processing on these micrographs. Scanning electron microscopy (SEM) analyses were performed using a JEOL JSM-7001F with an energy-dispersive X-ray...
Therefore, the black spots in the Fe, Co, and Ni samples were determined to be MLG. In contrast, for the Cu sample, a broad peak corresponding to a-C was obtained on the entire surface. From the observation using transmitted light, the black spots in the Fe, Co, and Ni samples were determined to be MLG. In contrast, for the Cu sample, a broad peak corresponding to a-C was obtained on the entire surface.

The MLG coverage increases with increasing thickness of MLG. Consequently, the domain size roughly increases with increasing thickness of MLG. Therefore, the domain size and surface coverage of MLG vary with both thickness of C and Ni. For t_C ≥ 20 nm, the domain size and surface coverage of MLG were determined by the supplied amount of C and the amount of C that Ni can dissolve. We note that the D band intensity in the Raman spectra did not change with t_C until the surface was covered by a-C. Figure 3b shows that the MLG domain size roughly increases with increasing t_C except for t_C = 3 nm. The sample with t_C = 3 nm and t_Ni = 1000 nm exhibits the maximum domain size of 2.5 μm. This means that adding a small amount of C to a thick Ni layer is effective to obtain MLG with a large domain. Figure 3c shows that the MLG coverage increases with increasing t_C. The coverage does not depend on t_Ni for t_C ≤ 20 nm, whereas it increases with increasing t_Ni for t_C ≥ 40 nm. The maximum coverage of approximately 50% is obtained for t_C = 60 nm and t_Ni = 1000 nm. This is likely because a thicker Ni layer can dissolve more C atoms. In addition to increasing t_C and t_Ni, optimizing the cooling rate will be also effective in improving the surface coverage. Thus, the domain size and surface coverage of MLG were determined by the supplied amount of C atoms and the amount of C that Ni can dissolve. We tried to measure the MLG thickness using atomic force microscopy; however, it was difficult to identify MLG due to the Ni surface roughness. Considering that the amount of precipitated MLG depends on the solid solution amount of C in Ni, the MLG thickness will show a similar tendency to the surface coverage of MLG (Figure 3c).

Generally, the D band intensity of MLG increases as the synthesis temperature decreases. Because the synthesis temperature of the current MLG is as low as 400 °C, disorders in MLG would be responsible for the large D band intensity (Figure 2e). The MLG domains are the largest for the Ni sample. Figure 2f,g shows that the domain size of the Ni sample is approximately 1 μm. Thus, MLG was synthesized at a low temperature of 400 °C by sputtering using metal catalysts with high solid solubility of C.

We investigated the effect of the thickness of C and Ni (t_C and t_Ni) on MLG’s growth properties. We note that t_C corresponds to the product of C deposition time and deposition rate (2.2 nm/min). Figure 3a shows that the D band intensity in the Raman spectra did not change with t_C until the surface was covered by a-C. Figure 3b shows that the MLG domain size roughly increases with increasing t_C except for t_C = 3 nm. The sample with t_C = 3 nm and t_Ni = 1000 nm exhibits the maximum domain size of 2.5 μm. This means that adding a small amount of C to a thick Ni layer is effective to obtain MLG with a large domain. Figure 3c shows that the MLG coverage increases with increasing t_C. The coverage does not depend on t_Ni for t_C ≤ 20 nm, whereas it increases with increasing t_Ni for t_C ≥ 40 nm. The maximum coverage of approximately 50% is obtained for t_C = 60 nm and t_Ni = 1000 nm. This is likely because a thicker Ni layer can dissolve more C atoms. In addition to increasing t_C and t_Ni, optimizing the cooling rate will be also effective in improving the surface coverage. Thus, the domain size and surface coverage of MLG were determined by the supplied amount of C atoms and the amount of C that Ni can dissolve. We tried to measure the MLG thickness using atomic force microscopy; however, it was difficult to identify MLG due to the Ni surface roughness. Considering that the amount of precipitated MLG depends on the solid solution amount of C in Ni, the MLG thickness will show a similar tendency to the surface coverage of MLG (Figure 3c). Generally, the surface of the MLG precipitated from metals has only C–C bonds and no
functional group such as C−O bonds. Therefore, the current MLG surface also seems to have no functional groups and consists of C−C bonds.

We investigated the detailed cross-sectional structure of the sample for $t_C = 60$ nm and $t_{Ni} = 1000$ nm, which has the maximum MLG coverage (Figure 3). The bright-field TEM images and EDX mapping in Figure 4a−c show that the MLG domains with various sizes are locally formed on the Ni layer, which is consistent with the optical micrograph (Figure 3a). The Ni concentration in the MLG domain is below the detection limit of EDX as in the other precipitation methods. Further investigations into the cooling rate, RF power, and Ni structure will allow us to improve the domain size and surface coverage or control the domain location. The findings in this study should encourage studies exploring the low-temperature synthesis of MLG using a simple sputtering method.

CONCLUSIONS

This sputtering method using metal catalysts enabled MLG to be formed at 400 °C. The domain size and surface coverage of MLG were determined by the supplied amount of C atoms and the Ni layer thickness associated with the solid solution amount of C. The maximum domain size and surface coverage of MLG were approximately 2.5 μm and 50%, respectively. The authors declare no competing financial interest.

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Figure 3. Effects of $t_C$ and $t_{Ni}$ on the growth morphology of MLG. (a) Nomarski optical micrographs for the matrix composed of $t_C$ and $t_{Ni}$. (b) Domain size and (c) surface coverage of MLG as a function of $t_C$, which were calculated by binarizing the optical micrographs.
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