

# Uniformity of Graphene CVD Growth Depending on the Thickness and Domain Structure of Epitaxial Metal Films

Shigeo Yoshii, Katsuya Nozawa, Kenji Toyoda and Nozomu Matsukawa

Advanced Technology Research Laboratories, Panasonic Corporation  
3-4 Hikaridai, Seika, Kyoto 619-0237, Japan  
Phone: +81-774-98-2580 E-mail: yoshii.shigeo@jp.panasonic.com

## 1. Introduction

Many efforts have been made toward achieving large-scale and high-quality graphene growth. Chemical vapor deposition (CVD) on metal surface is suitable for making large area graphene, nevertheless the quality of graphene seems to depend on the underlying metal surface [1,2]. Some metals have crystal surfaces which are nearly lattice matched both to graphene and *c*-plane sapphire (Fig. 1) [3]. Therefore, epitaxially grown metal film on sapphire substrate would give an ideally oriented surface for graphene growth. In this approach, the effect of thickness and structure of metal film on graphene growth is of great interest from the viewpoint of elucidating the growth mechanism and achieving high-quality graphene. Ago et al. have already reported on graphene growth on epitaxial Ni and Co [4], but its dependence on metal thickness or structure has not been reported. In this study, we investigated the uniformity of graphene growth by employing three metals with different crystal structures, Ni (fcc), Ru (hcp) and Co (fcc at high temperature and hcp at R.T.), and varying the Ni film thickness.

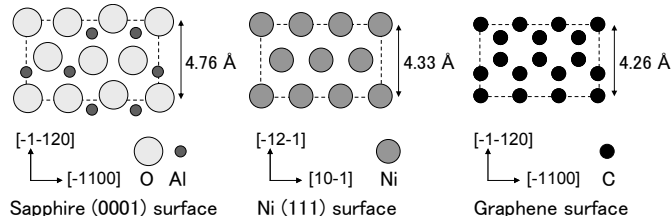


Fig. 1 In planar relationship for the surfaces of sapphire (0001), Ni (111) and graphene.

## 2. Experimental

A 30 nm thin Ru film was sputtered on a *c*-plane sapphire substrate. Ni and Co were deposited on sapphire by electron-beam evaporation. The Ni film thickness was varied from 40 to 300 nm. Substrates were placed in a furnace and annealed in hydrogen for solid phase epitaxial recrystallization. Then a mixture gas of 1 to 5% methane and hydrogen was introduced into the furnace and graphene layer was grown on the metal surface. Recrystallization and CVD were performed at temperatures from 900 to 1100°C. The crystal structures of metal films were examined with X-ray diffraction (XRD) analysis. Samples after CVD were investigated with Raman spectroscopy, optical microscopy, atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM).

## 3. Results and Discussion

XRD analysis revealed that epitaxial metal films were grown on *c*-plane sapphire surface in all cases of Ni, Ru, and Co. Figure 2 shows the XRD patterns for Ru (hcp) film after hydrogen anneal. The intense single (0002) pole and six-fold sharp (10-13) poles in the pole figures evidenced the single domain nature of the Ru film. Co (hcp) film had rather broad peaks supposedly due to its fcc-hcp phase transition. In the case of Ni (fcc) film, six (200) poles indicated the twin structure due to the two types of fcc stacking sequences, *ABCABC...* and *ACBACB...*

CVD of methane-hydrogen mixture was performed using the epitaxial metal films. Raman spectra with clear G and 2D peaks were obtained for all of Ni, Ru and Co films (Fig. 3). Cross-sectional HRTEM and AFM revealed few- or multi-layer graphene grown on epitaxial metal surfaces, and lattice-matched interface between metal film and sapphire substrate (Fig. 4). Notably the Co film, which experienced phase transition, retained its surface flatness even after CVD process.

There are two major possible mechanisms for graphene growth on metals. One is surface catalytic synthesis at high temperature and the other is segregation in cooling. While the former generally does not depend on metal film thickness, the latter strongly depends on it. The amount of segregating carbon is limited by the total amount of diffused carbon in metal, which can be controlled by film thickness.

Figure 5 shows the optical microscope images and surface morphology by Nomarski optics for varied Ni film thickness. The maximum graphene layer number that can be generated by segregation is also indicated in Fig. 5. The 40 nm Ni film had flat surface in local, but many defects with tens of micrometer size were observed. This thin Ni film seems unable to withstand the thermal stress and carbon embrittlement in CVD process. The 70 and 150 nm Ni had rather smooth surface and grain boundaries between two stacking domains were observed. The thicker 300 nm film had a rough surface with many dark grains. We mapped the Raman spectra on the 150 nm Ni and found that the G peak is greatly intensified at the grain boundaries (Fig. 6(b)). Intense G peak was also observed at the dark grains on the 300 nm Ni. These results suggest that the segregation, which depends on the metal film thickness, contributes to the graphene growth on Ni, and the segregation occurs preferentially at grain boundaries, resulting in non-uniformity in growth.

In the case of Ru, a thin 30 nm film showed no damage after CVD (Fig. 5(g)). Clear G and 2D peaks were observed even though the maxim graphene layer number by segregation was less than one. No grain boundary was found in this single domain film and Raman mapping showed much uniform distribution compared to that of Ni (Fig. 6). The surface catalytic synthesis also contributes to the graphene growth and non-uniform segregation can be effectively prevented by controlling the metal film thickness and removing grain boundaries.

### 3. Conclusions

We have investigated the graphene growth and its dependence on the thickness and structure of epitaxial metal films. Locally enhanced segregation at grain boundary has been found to be one of the major sources of non-uniformity. Uniform graphene growth is achieved with a single domain thin Ru film, in which segregation is restrained and grain boundaries are eliminated. Suppression of local segregation is essential in high-quality graphene growth.

### References

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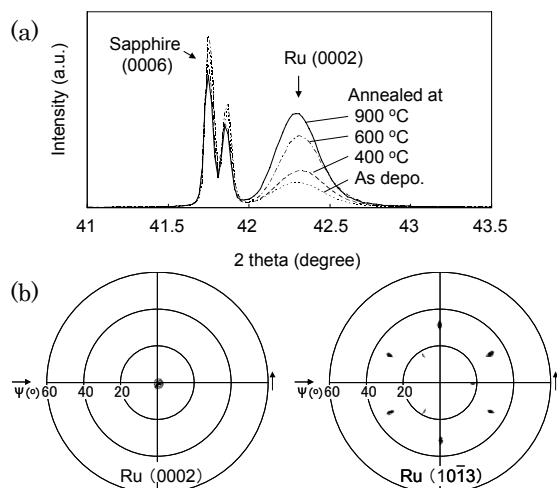


Fig. 2 XRD patterns of Ru film on sapphire. Theta-2 theta scan (a), and pole figures for (0002) and (10-13) reflections (b).

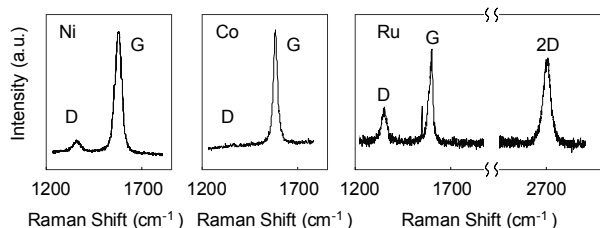


Fig. 3 Typical Raman spectra measured for graphene layers on epitaxial Ni, Co, and Ru films.

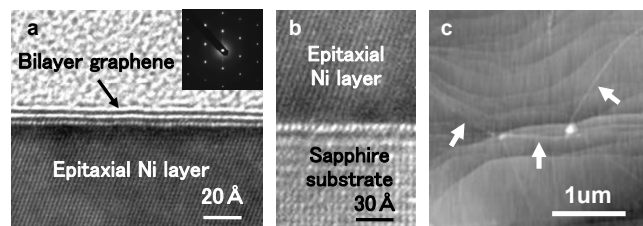


Fig. 4 HRTEM images of (a) bilayer graphene on Ni film, (b) Ni / sapphire interface, and (c) AFM image of Co surface with graphene layer. Arrows in (c) indicate the wrinkle structure [5] of multi-layer graphene crossing over the step and terrace structure.

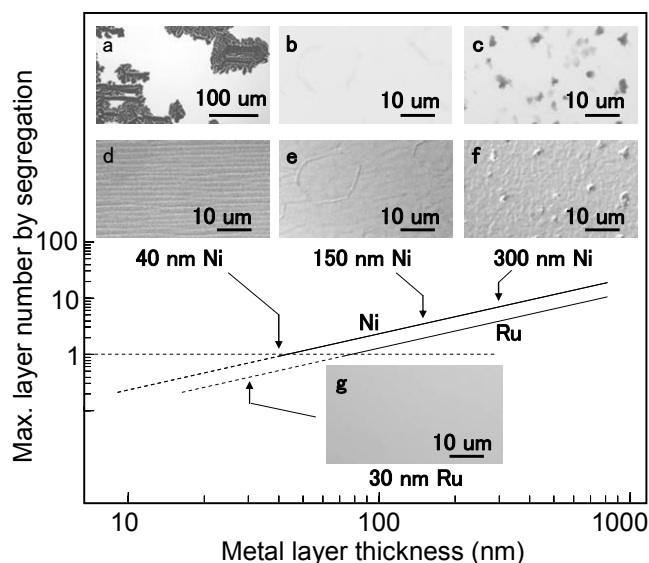


Fig. 5 Surface morphology of epitaxial films after CVD. The optical microscopy images (a)-(c), and the Nomarski interference images (d)-(g). Lines show the maximum graphene layer number that can be generated by segregation for Ni and Ru.

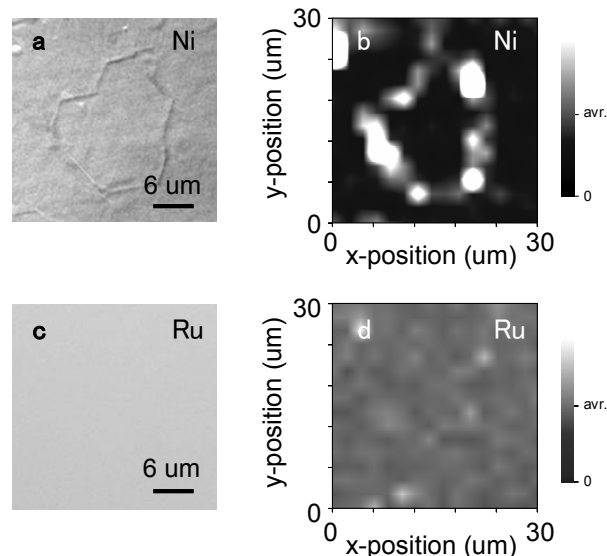


Fig. 6 Nomarski images (a,c), and Raman mapped images showing G intensity distributions (b,d), after CVD. (a) and (b) are measured at the corresponding site (grain) on 150 nm Ni film. (c) and (d) are measured on Ru film.