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Synthesis of Carbon Thin Films using Plasma CVD with Nano-thickness Catalysts

ナノ膜厚触媒を用いたプラズマCVDによる炭素薄膜合成

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Many researchers have been succeeded to produce high quality of single layer graphene by using Cu foil (100nm to μm thickness) catalyst. In this study, we tried to use nano-thickness catalysts with which visible light can pass thorough the films and deposited carbon films by RFCVD on the nano-thickness catalysts. By using nano-thickness catalysts, direct synthesis of transparent and conductive graphitic films on glass substrate is expected because enhancement of surface migration of carbon atoms is expected in RFCVD by ion bombardment at low substrate temperature. Catalytic synthesis of graphitic carbon films were confirmed to be enhanced on Cu nano-thickness catalysts compared with without catalysts.

1. Introduction

Graphene [1] has higher electric conductivity and higher transmittance even with atomic layer thickness, which can be expected as a material for transparent and conductive film. High quality and single layer graphene was reported by using Cu foil catalyst [2] of few carbon solubility of 0.008 weight% at ～1084℃[3]. High-carbon-solubility catalyst Ni (～0.6 weight% at 1326℃ [4]) precipitate multi-layer (1～10 layers) graphene [5,6]. Plasma chemical vapor deposition (PCVD) using Cu foil catalyst have been reported to synthesize graphene at low temperature[7] and large area deposition by microwave plasma and roll to roll process [8]. T. Harigai *et al*., reported nano-thickness DLC film properties which were formed by pulsed radio frequency CVD (RFCVD) [9]. Furthermore, by using nano-thickness catalysts, direct synthesis of graphene transparent and conductive film on glass substrate is expected because enhancement of surface migration is expected in RFCVD by ion bombardment at low substrate temperature. In this study, nano-scale-thickness catalysts, those thickness could pass through visible light, were investigated for the catalytic synthesis of carbon films by RFCVD.

2. Experimental

Cu or Ni catalysts were deposited in 10 nm thickness on glass substrates by DC magnetron sputtering method. Sputtering condition were Ar flow rate of 28 sccm, sputtering pressure of 0.8 Pa, DC discharge current of 20 mA and pre-sputtering time of 5 min. RFCVD conditions were discharge pressure of 10 Pa, RF power of 100 W, C_2H_2 gas flow rate of 89 sccm. Deposition rate of carbon film was 3.3 nm/sec for this RFCVD condition. CVD durations were varied in 0.6, 0.9, 1.2 and 1.5 sec. RFCVD pressures were varied in 10, 20, 40 and 60 Pa with the deposition durations of 0.9, 0.45, 0.22 and 0.11 sec, respectively to obtain films in same thickness of 3 nm. Deposited carbon films were characterized by Raman spectroscopy (laser wavelength of 532.08 nm) and four contact sheet resistance measurement. Raman shift curves were analyzed by peak separation based on the 2 peak separation method[10].

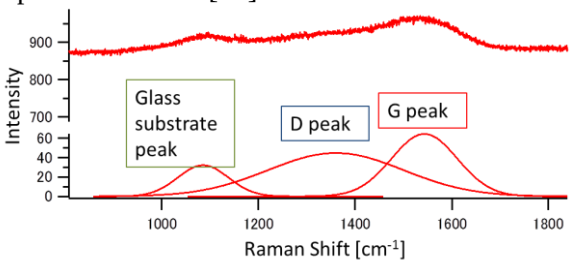

Fig.1. (upper) A typical Raman shift curve of carbon films deposited by the RFCVD with on Ni catalyst of 1.5sec, and (lower) separated peaks of G, D peaks and glass substrates.

3. Results

Figure 2 and Fig. 3 shows plots of G peak locations and D/G ratios versus RFCVD pressures of 10, 20, 40 and 60 Pa with or without Cu catalyst. With using Cu catalyst, all G peak locations shifted to higher wave number and D/G ratios increased compared with deposited films without catalyst.

Figure 4 and Fig. 5 shows G peak location around 1555 cm^{-1} and D/G ratio around 1.2 for the carbon films deposited on Cu and Ni catalysts. G

peak location and D/G ratio of the carbon films showed similar values for the Cu and Ni catalysts deposited for between 0.9 sec and 1.5 sec, but not for 0.6 sec. Sheet resistance shows almost same catalysts film conductivity before RFCVD (Cu 10nm 18.67 to 19.08Ω/□, Ni 10nm 137.3 to 147.7Ω/□) in each CVD duration time.

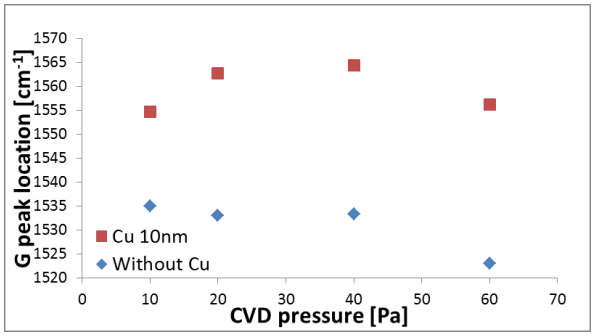

Fig. 2. Plots of G peak vs. CVD pressure (10, 20, 40, 60Pa) of films with and without Cu catalyst.

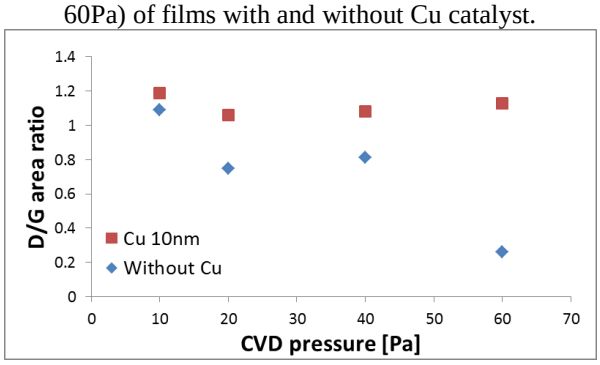

Fig. 3. Plots of D/G area ratio vs. CVD pressure (10, 20, 40, 60Pa) of films with and without Cu catalysts.

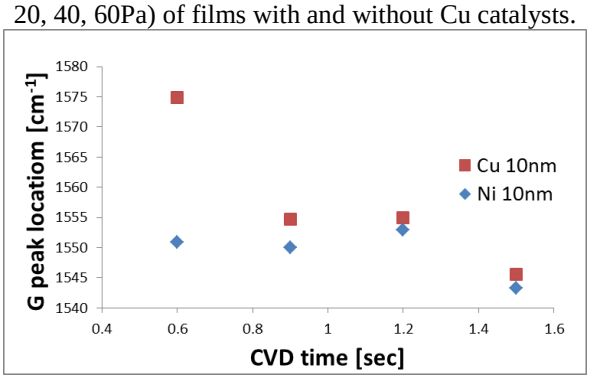

Fig. 4. Plots of G peak location vs. RFCVD time (0.6, 0.9, 1.2, 1.5sec) of films on Ni and Cu catalysts.

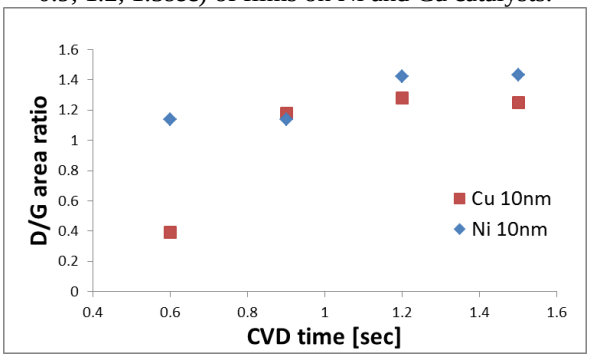

Fig. 5. Plots of D/G area ratio vs. RFCVD time (0.6, 0.9, 1.2, 1.5sec) of films on Ni and Cu catalysts.

4. Discussion

According to 2 peak separation of Raman spectra in DLC[8], Fig. 2 and Fig. 3 shows carbon films on Cu catalysts have higher G peak shift and higher D/G ratios compared with the films on substrates without catalyst, which indicates nano-crystalline graphite were catalytically synthesized on Cu catalysts. However, D/G area ratio and G peak shift were similar on Ni and Cu for the carbon films deposited between CVD time of 0.9 to 1.5 sec. These results cannot be explained by different catalytic effect on Cu[2] and Ni[5]. One of the possibilities is that substrates affected efficiencies of Ni and Cu nano-catalysts.

5. Conclusion

RFCVD synthesis of nano-thickness carbon films on nano-thickness Ni and Cu catalysts were investigated. In various CVD pressure of 10 to 60 Pa, G peak shifted to higher wave number and D/G ratios increased on Cu catalysts compared with without catalysts in each CVD pressures. These results suggest that Cu catalysts enhanced formation of nano-crystalline graphite. Carbon films deposited on Ni and Cu showed similar G peak shifts and D/G ratio for the CVD time of 0.9sec to 1.5sec. One of the possibilities is that substrates affected efficiencies of Ni and Cu nano-catalysts.

Acknowledgments

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