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Pengaruh Pemanasan Terhadap Morfologi Permukaan dan Ukuran Grain pada Lapisan Tipis Tembaga Sebagai Katalis pada Penumbuhan Graphene

A Study of the Effect of Thermal Annealing on the Morphology Surface and Grain Size of Thin Copper Films as Catalyst for Graphene Growth

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ABSTRACT

The effect of thermal annealing on the morphology surface and grain size of thin copper films was studied. The purpose of this study is to find an optimal annealing condition in obtaining a copper catalyst, having a smooth surface with a large grain size. Such catalyst is potential to grow a high quality graphene film. In this work, the copper film (99.99+ % purity; 500 nm thick) was employed by varying annealing temperature (450-900 °C), annealing time (0-1200 min) and hydrogen flow rate (0-100 sccm). These copper catalysts were further studied by means of XRD, SEM and EDS analysis to know their structural properties. XRD results revealed that this copper film has a good nanocrystalline cubic structure, dominated by (111) plane. SEM results showed that the 900 ^{o}C- annealed copper film has larger grain size (~ 1.3 µm) than the others. EDS analysis showed the presence of copper oxide peaks on the annealed copper under hydrogen-free atmosphere, indicating the importance of hydrogen gas for removing the copper oxide impurities. Based on those studies above, the optimal annealing condition for obtaining a copper substrate with the smooth surface and large grain size is by annealing at 450 °C for 20 hours under hydrogen flow rate of 50 sccm.

Keywords : Thin copper film, Thermal annealing, grain size.

ABSTRAK

Telah dilakukan penelitian tentang pengaruh pemanasan terhadap morfologi permukaan dan ukuran grain pada lapisan tipis tembaga sebagai katalis pada penumbuhan graphene. Penelitian ini bertujuan untuk menemukan kondisi optimal pada katalis tersebut dalam persiapan penumbuhan graphene. Dalam penelitian ini, lapisan tipis tembaga yang digunakan memiliki kemurnian 99.99+ % dan ketebalan 500 nm telah divariasikan pada suhu pemanasan (450-900 °C), waktu pemanasan (0-1200 min) dan laju aliran hydrogen (0-100 sccm). Morfologi pada sampel-sampel yang dihasilkan telah diuji dengan menggunakan peralatan seperti XRD, SEM and EDS analysis. Hasil pengujian XRD menunjukkan bahwa sampel tersebut memiliki *nanocrystalline cubic structure* yang baik dengan didominasi oleh bidang (111). Hasil pengujian SEM menunjukkan bahwa sampel yang dipanaskan pada suhu 900 ^{o}C memiliki ukuran grain yang lebih besar size (~ 1.3 µm) dibandingkan dengan sampel

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lainnya. Hasil analisis EDS menunjukkan adanya puncak-puncak tembaga oksida pada sampel yang tidak dialirkan gas hydrogen, yang berarti bahwa gas hidrogen sangat berperan dalam mengeliminir impurity dari tembaga oksida. Berdasarkan hasil-hasil pengujian di atas maka kondisi optimal dalam pemanasan lapisan tipis tembaga sebagai katalis pada penumbuhana graphene adalah pemanasan pada 450 °C selama 20 jam dengan laju aliran hydrogen sebesar 50 sccm.

Kata Kunci : Lapisan tipis tembaga, Pemanasan, morfologi permukaan, Ukuran grain.

INTRODUCTION

In the last few years, copper foil has attracted considerable interest in both academic and industrial communities since the report of large-area graphene thin films for conductive and transparent electrodes (Bae *et al*., 2010; Kim *et al*., 2009 and Li *et al*., 2009). However, some practical complications are involved when using copper foil as the catalyst. For example, it takes quite a number of hours to etch away the copper foil as the thickness of a copper foil is generally in the range of tens micrometres. The etching of different Cu catalyst thicknesses (12.5, 25 and 50 μm) was conducted by Xuesong Li, *et al*. [4] showing that the etching time was a function of thickness. Furthermore, it normally requires a transfer step which uses PMMA as the transfer agent, which is very hard to wash off completely once the graphene film is transferred to a substrate and can lead to contamination to some degree.

To eliminate the transfer step, much thinner (hundreds of nanometres) copper thin films are more desirable. These copper thin films can be easily deposited to selected substrates and be etched away quickly without the need for a transfer step. Annealed copper foils preferentially form as a Cu(100) crystalline face (Wofford *et al*., 2010), while thermally grown copper thin films lead to prefer in the Cu(111) crystalline orientation. These different crystalline structures lead to different graphene growth which has been reported by Ruoff etc. Further work by Pasupathy [6] also reported that a single crystal Cu(111) face is superior to a Cu(100) face to grow more uniform graphene sheets. However, thermally grown copper thin films form small nanodomains and require an annealing step to form large domains which in turn, determine the dimensions of the graphene sheet and electrical properties of the graphene films. Therefore, it is especially important to understand the exact crystal structure evolution of copper

thin films during the pre-treatment before the graphene growth.

MATERIAL AND METHOD

To prepare a catalyst with high quality for growing graphene, a kind of copper, i.e. thin copper film (99.99+ % purity; 500 nm thick), was employed for studying the effects of thermal annealing on its microstructure, by varying annealing temperature (450-900 °C), annealing time (0-1200 min) and hydrogen flow rate (0-100 sccm). All these experiments were conducted in an Atomate CVD furnace (Fig. 1) by introducing a mixture of H_2/Ar (50 and 100 sccm, respectively) gas under a pressure of 500 mTorr, except for the study of the variation of hydrogen flow rate. The introduction of hydrogen gas is desired to reduce copper oxides which may occur on the surface, while argon gas is applied to remove H_2O steam as reaction products or unwanted gases. Properties of the studied samples were characterised by using X-ray diffraction (XRD) for the crystal structure and scanning electron microscopy (SEM) for the morphological surface, while EDS analysis was used to confirm the presence of copper oxide on the hydrogen-free flowed sample

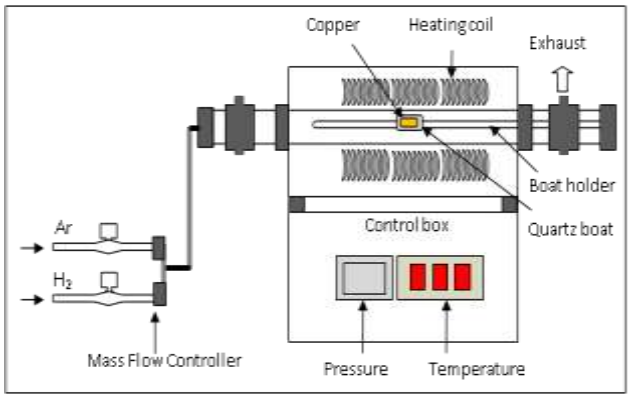

Figure 1. Schematic of the Atomate CVD furnace used for annealing the copper.

RESULT AND DISCUSSION

XRD measurements were used to study the effect of annealing on the microstructure of copper substrate. In this technique, a CuKα radiation source (λ = 1.54056 Å) was employed and the diffraction patterns were recorded by varying diffraction angle (2θ) in the range 30˚ to 80˚. XRD patterns of the as-evaporated thin copper films (Fig. 2) with three major peaks at 2θ (degrees) values of 43.4°, 50.6° and 74.2° corresponding to reflections from the (111), (100) and (110) planes are well defined. All the diffraction peaks measured in the 2θ range correspond to the face-centered cubic (FCC) structure of copper with lattice constant a = 3.615 Å and is in good agreement with the standard data card (JCPDS Card No. 85-1326) value (Swanson, 1953). The sharpness of the diffraction peaks suggests that the substrate is well crystallized. Moreover, the absence of copper oxide (i.e. CuO, Cu_2O) peaks

indicates the high quality of prepared samples.

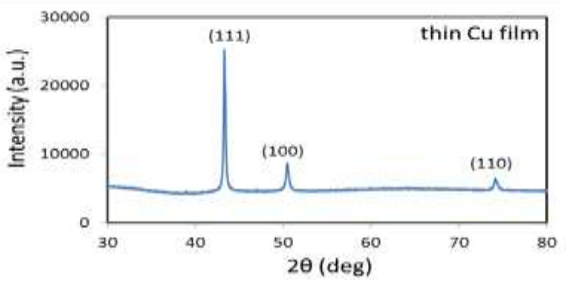

Figure 2 XRD spectra of the as-evaporated thin copper film

Effect of Annealing Temperature

Five different annealing temperatures (450, 600, 700, 800, 900 ^{o}C) for the fixed time and hydrogen flow rate of 1 hour and 50 sccm.were employed to study the effect of annealing temperature on the microstructure of thin copper substrate. These samples were characterised by using XRD (Fig. 3a) and SEM (Fig. 3b).

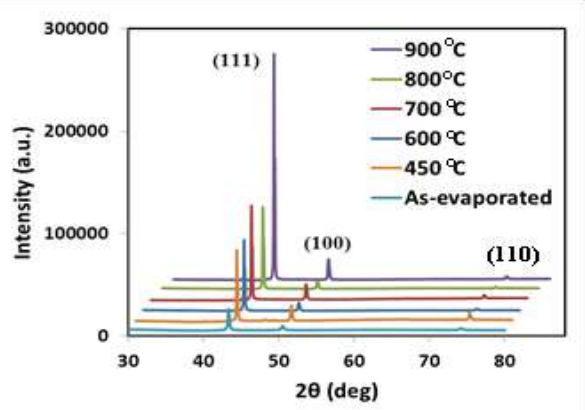

Figure 3a. XRD profiles of the thin copper films annealed at different temperatures

Figure 3a shows XRD profiles of the as-evaporated and annealed thin copper films with three major reflections from (111), (100), and (110) planes at the angle of 43.4°, 50.6° and 74.2°, respectively. From this figure, it is found that the diffraction peak of (111) plane on the samples is more intense than that of (100) and (110) planes. This observation indicates that the crystal structure with a (111) plane is more favourable than the others. However, the intensity of this plane increases after annealing, indicating the formation of larger grain structures, consistent with the previous report by Vinci et al. (Zielinski *et al*., 1994). A very strong (111) intensity is detectable when the sample is annealed at 900 ^{o}C. This peak increase is due to further re-crystallisation with a much larger grain size. On the other hand, the peak of the (110) plane exhibits no significant change indicating that the thermal annealing treatment does not cause a formation of other grain textures.

To confirm the change of (111) diffraction peaks on the thin copper film, observations were made in the SEM images of the films. Figure 3b shows that a noticeable grain growth on the thin copper films is clearly observed after annealing at temperatures above 700 ^{o}C. In fact, at 800 ^{o}C, grain structures clearly appear with a dominant size of around 0.6 µm. A much larger grain size of around 1.3 µm occurs at 900 ^{o}C. This observation confirms that it is the large grain size that is strongly associated with the high intensity diffraction peak, shown in Figure 3a.

Thus, it is clear that annealing temperature is a critical factor affecting the structure of the copper films due to grain-boundary diffusion at high temperatures (Thouless *et al*., 1993). Our observation of the evolution of thin copper film morphology from 450 to 900 °C indicates that higher annealing temperatures lead to larger grain size as shown in Figure 3b.

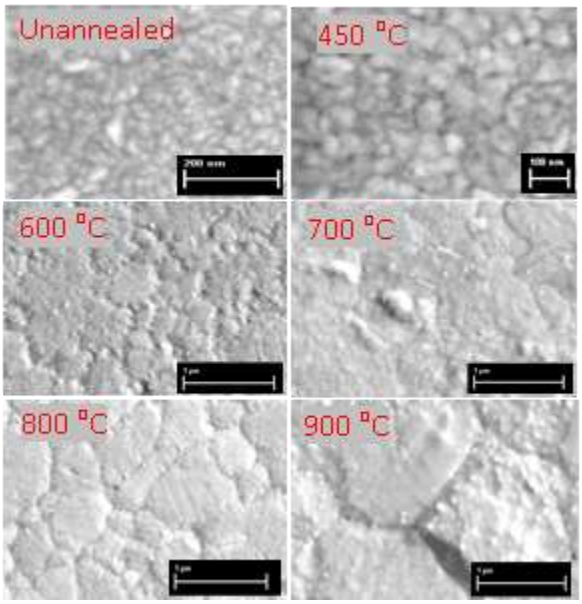

Figure 3b SEM images of the thin copper films annealed at different temperatures.

Effect of Annealing Time

In order to study the effect of annealing time on the microstructure of copper catalysts, thin copper films were further studied by annealing for various annealing times (0, 1, 3, 5, 10, and 20 hours) at the fixed temperature and hydrogen flow rate of 450 °C and 50 sccm. The main reason behind the selection of the low annealing temperature was that the film was evaporated on a glass substrate that undergoes mechanical changes over 450 °C. These samples were characterised by using XRD (Fig. 4a) and SEM (Fig. 4b).

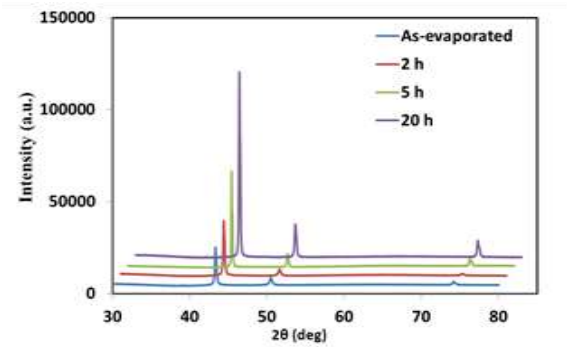

Figure 4a. XRD profiles of the copper films annealed for different times.

Figure 4a shows XRD patterns of the samples annealed for three different times of 2, 5 and 20 hours. In this figure, it appears that the intensity of (111) diffraction peak systematically increases with increasing annealing time. This is an indicator that increased recrystalisation occurs on the samples annealed for longer times.

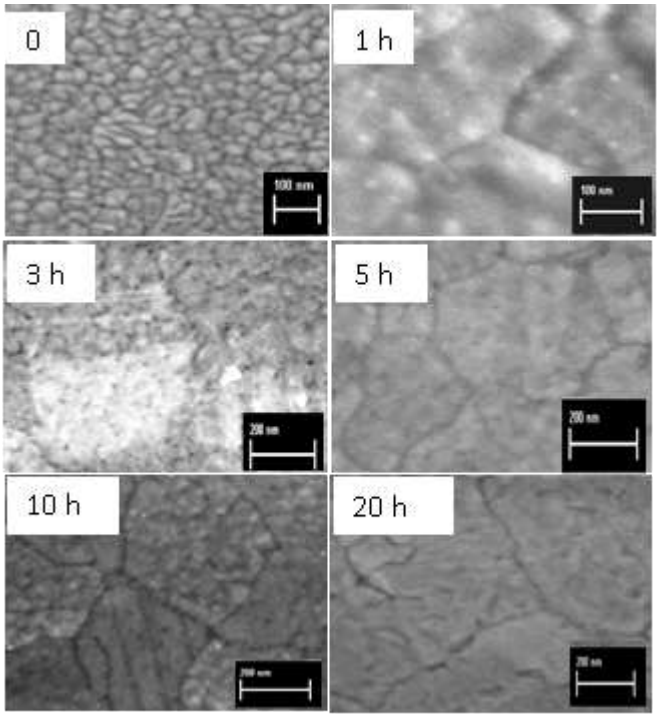

Figure 4b. SEM images of the copper films annealed for different times.

Figure 4b shows a series of SEM images with magnification of 250000x indicating the morphology at different reaction stages corresponding to the different annealing times. From the micrographs in Figure 4b, it appears that the grain size develops with increasing annealing times. The increase of grain dimension is about 8 to 18 times the original size with the largest grain size of ~ 680 nm, seen on the 20 hour annealed sample.

Effect of Hydrogen Flow Rate

To determine the influence of hydrogen gas on the formation of morphological structure on copper's surface, the copper substrate was studied by annealing under various flow rates of 0, 5, 10, 25, 50 and 100 sccm with a fixed annealing temperature and time of 450 ^{o}C and 1 hour, respectively. The goal of this study is to find an optimal hydrogen flow rate for resulting in a smooth surface of the substrates.

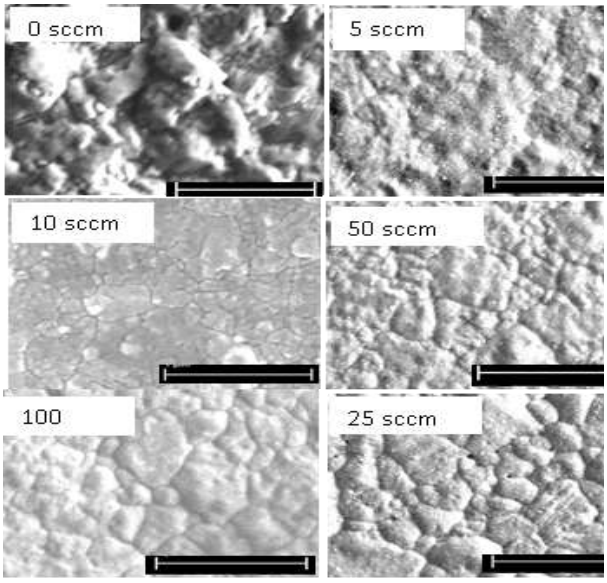

Figure 5 SEM images of thin copper film at 450 ^{o}C for 1 hour under different flow rates of hydrogen gas (scale bar: 1 µm).

Figure 5 shows that no significant development of the grain size is observed with increasing the flux of hydrogen gas. However, the grains are well-defined with irregular shapes and sizes when introducing a hydrogen flow rate above 10 sccm. The grains are not clearly observable on the samples introduced with 5 sccm and without hydrogen gas, and the hydrogen-free treated film surface is much rougher than that of the 5 sccm-treated surface. This roughness may be caused by the presence of a thin oxide layer. This study shows that the 1 hour-treated hydrogen flow rates do not form a larger grain, meanwhile, the large grain size can facilitate the growth of large graphene flakes (Mattevi *et al*., 2011). In comparison, the grain size of the 20 hours-annealed thin Cu film with the fixed hydrogen flow rate of 50 sccm (see Figure 4b) was much larger than that of the 1 hour-annealed thin Cu film with the varied hydrogen flow rates (see Figure 5). This reveals that the best condition to prepare the thin copper film as catalyst for graphene growth is by annealing at the temperature of 450 ^{o}C for 20 hours under the hydrogen flow rate of 50 sccm.

To confirm the presence of a thin oxide layer on the hydrogen-free flowed thin Cu film, EDS analysis was applied (see Figure 5). In this method, two different energies of 2 and 10 keV were applied in order to identify the element contents in different depths on the copper bulk, with the higher energy electron beam probing deeper into the bulk of the material (Giedt *et al*., 1988 and Miculescu *et al*., 2011). By applying the 10 keV energy, the presence of carbon, oxygen and copper elements is detected as shown in Figure 6. Interestingly, when applying the 2 keV energy, the content of carbon and oxygen elements increases, while the copper content decreases. This change is due to the formation of both elements on the copper surface, indicative of a thin copper oxide layer and amorphous carbon layer being formed on the surface. To identify the kind of copper oxide, XRD was used. In this XRD experiment, two low extra peaks are found at 36.4^{o} and 60.0^{o} indicative of resulting from the copper oxides of Cu_2O [111] and Cu_2O [220], respectively, as seen in Figure 7 (Yin *et al*., 2005).

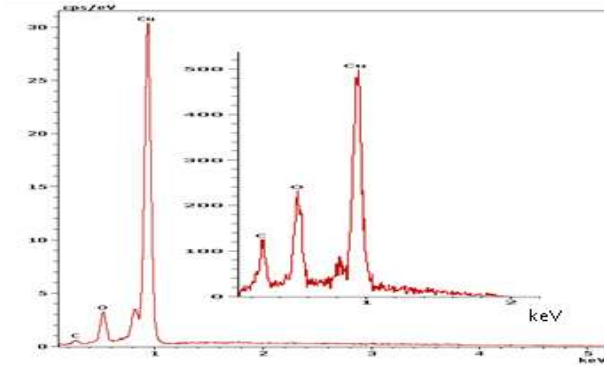

Figure 6a EDS analysis of the thin copper film annealed at 450 ^{o}C under the hydrogen-free atmosphere.

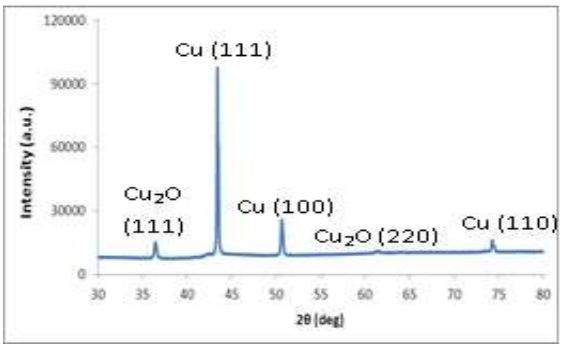

Figure 6b XRD profile of the thin copper film annealed at 450 ^{o}C under the hydrogen-free atmosphere.

Crystallite and Grain Sizes

To get a deeper insight into the influence of annealing on the copper microstructure, the crystallite size of the grains in thin copper films was calculated by using the Debye-Scherrer formula as follows (Patterson, 1939):

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

where, λ is the wavelength of the incident X-rays (0.154056 nm for Cu $K\alpha_1$), β the half width of diffraction peak measured in radians, and θ the diffraction angle. While, the determination of grain sizes on the films was obtained by using the standard intercept count method of ASTM E112, which is based on the number of grain boundary intersections per unit length, P_L. This unit is a random test line that produces on statistically representative sections (Abrams, 1971). Mathematically, it is defined as:

$$P_L = \frac{P_i}{L_T / M} \qquad (2)$$

where P_i is the number of grain boundary intersections counted on the test line, L_T is the total test length and M is the magnification.

In this study, the calculation of crystallite and grain sizes was carried out on thin copper films annealed at different temperatures (see subsection 3.1). The average crystallite and grain sizes calculated are plotted in Figure 7.

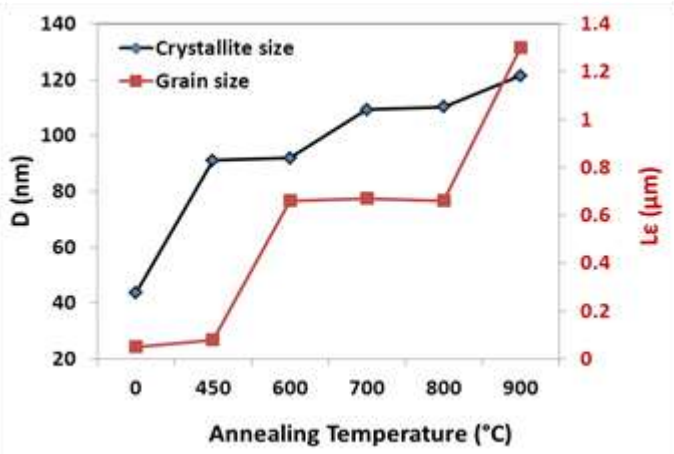

Figure 7 Crystallite and grain sizes on thin copper film as a function of annealing temperature.

Figure 7 clearly shows that the crystallite sizes increase significantly after annealing and gradually grows bigger with increasing annealing temperature, while the significant increase of grain sizes occurs

after annealing beyond 450 ^{o}C. The average crystallite size resulted is ~ 100 nm. This result shows that annealing provides larger crystallites compared to the original size. The grains of the unannealed thin Cu film are observed to be ~ 0.05 µm in size. An increase of grain size occurs when annealed beyond 600 ^{o}C and more significantly increases when annealed at 900 ^{o}C with ~ 1.3 µm in size.

By studying the effect of the annealing temperature, annealing time and hydrogen flow rate on thin copper film in forming a grain structure, a combination of the parameters for was selected to be an annealing temperature at 450 ^{o}C for 20 hours under hydrogen flow rate of 25 sccm. The choice of this low temperature is due to the use of glass as a substrate in evaporating thin copper film. Glass undergoes mechanical changes, such as bending, when annealed above 450 ^{o}C and even melts when annealed above 550 ^{o}C.

This paper has presented a study of the effect of thermal annealing on the morphology of thin copper film as catalyst for graphene growth. As-evaporated thin copper film was annealed with various temperatures, times, hydrogen flow rate for studying the change of structural and morphological properties. The film was annealed firstly at 450 to 900˚C for a time and hydrogen flow rate of 1 hour and 50 sccm, respectively, then for 1 to 20 hours at the fixed temperature and hydrogen flow rate of 450 ^{o}C and 50 sccm, and lastly under hydrogen flow rates of 0-100 sccm by selecting the temperature and time of 450 ^{o}C and 1 hour. Structural properties were studied by means of XRD, SEM and EDS analysis. The XRD results revealed that the copper type has a good nanocrystalline cubic structure, dominated by (111) plane. The SEM results show that the sample annealed at 900 ^{o}C has smoother surface morphology with uniform coverage and larger grain size (~ 1.3 µm) than the others. The EDS analysis showed the presence of copper oxide peaks on the annealed copper under hydrogen-free atmosphere This analysis indicates that the hydrogen gas is crucial for removing the copper oxide impurities.

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