Transport Properties and Sensing Responses of Platinum Nanoparticles/Graphene Structure Fabricated by Thermal Annealing Process
(Sifat Pengangkutan dan Tindak Balas Pengesanan Struktur Nanopartikel/Grafin Platinum melalui Proses Penyepuhlindapan Termal)

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ABSTRACT
The effects of the annealing temperatures and thicknesses on the shapes, sizes and arrangement of platinum (Pt) nanoparticles (NPs) on graphene and their sensing performance for hydrogen (H$_2$) detection were investigated. It shows strong dependency of the annealing temperatures and thicknesses on the properties of NPs. It was found that the proposed technique is able to form the NPs with good size controllability and uniformity even for thick deposited layer, thus eliminating the requirement of very thin layer of below 5 nm for the direct NP synthesis by evaporation or sputtering. The transport properties of Pt NPs/graphene structure and its sensing performance on H$_2$ at room temperature under various H$_2$ concentration were evaluated. The results showed an acceptable sensing response, indicating an innovative approach to fabricate Pt NPs embedded graphene for gas sensing application.

Keywords: Graphene; hydrogen; nanoparticles; platinum; sensors

INTRODUCTION
An obstacle for hydrogen (H$_2$) to be used as a new green energy source is due to the danger of explosion when its concentration in a mixture with air exceeds four percents (Crowl & Jo 2007; Hübert et al. 2011; Najjar 2013; Schmidtchen 2009; Sherif et al. 2003). The detection of H$_2$ gas leaks with a low-cost sensor operated in ambient condition is desirable for the societal acceptance. Platinum (Pt) has been shown as the promising catalytic metal for H$_2$ absorption (Crowl & Jo 2007; Hübert et al. 2011; Najjar 2013; Schmidtchen 2009). The absorption of H$_2$ into Pt leads to the breaking of the H-H bond and the formation of two H-Pt bonds. This makes it easier to remove an electron from each H atom, generating the formation of two H$^+$ ions from H$_2$. The reason why Pt is a good catalyst is that its capability to bind H$_2$ strongly enough, but not too strongly. Meanwhile, nanoparticle (NP) has been considered as an ideal structure for the gas sensing because of its large surface area which is needed to increase the sensitivity (Hübert et al. 2011; Schmidtchen 2009). Recently, graphene sheet (GS), a new class of two-dimensional (2D) carbon material, has attracted tremendous attention for the application in various fields owing to not only its high specific surface area but also its high chemical stability and excellent electrical conductivity (Avouris 2010; Kumar et al. 2015; Phan & Chung 2013; Rahman et al. 2014, 2013). Being a semimetal, the electronic configuration of graphene allows the electrons to propagate as the massless Dirac particles. Thus, the chemical bonding in graphene endows it with a high conductivity and its monolayer nature allows its π-conjugated system to be entirely exposed to external influences. It is widely reported that in an ultrahigh vacuum condition, that absorption events of the molecules onto graphene will change its electronic properties. Thus, by using graphene as the electrode in a Schottky diode, it is possible to modify the device characteristics through a chemical modulation of the electrode (Fu et al. 2016). This facilitates the development of a new type of sensing platform especially through the combination of metal-NPs such as silver (Ag) and reduced graphene oxide (rGO)
The controllability of annealing temperature and deposited film thicknesses and their effects on the properties of Pt NPs are studied. The sensing performance of the fabricated Pt NP/graphene structure is also investigated and discussed.

EXPERIMENTAL DETAILS

Figure 1 shows the schematic of the formation of Pt NPs and the fabricated sensor structure. As shown in Figure 1(a), the substrate is the chemical vapor deposition (CVD) grown single layer graphene on SiO$_2$/Si substrate (Graphene Laboratories, US). Pt thin film is deposited on graphene with the thicknesses of 6, 9, 12, and 15 nm by using plasma coater (GSL-1100X-SPC-12, MTI Corporation) with the base pressure of 5.8 Pa in the presence of argon (Ar) gas as shown in Figure 1(b). Subsequently, an annealing process is applied at different temperatures of 600, 700, and 800°C in order to force the Pt phase to rearrange into NP forms as shown in Figure 1(c). Finally, as shown in Figure 1(d), 55 nm-thick of gold (Au) interdigital electrode (IDE) is directly formed on top of the Pt NP/graphene structure through metal mask by conventional thermal evaporation. The performance of the fabricated sensor is measured using a homemade system as shown in Figure 2. Here, the sensor is kept in the gas chamber and tested at various H$_2$ concentrations. Nitrogen (N$_2$) is connected to the chamber for cycling test of gas sensing performance. Before the measurement is performed, the chamber is purged with N$_2$ at 200 sccm for 10 min to remove the air. The electrical characteristics are measured by the parametric measurement unit (Agilent Technologies B1500A).

RESULTS AND DISCUSSION

Figure 3 shows the FESEM images of the as-deposited and annealed Pt on graphene/SiO$_2$/Si. In a glance, the size of NP increases with the deposited thickness of Pt. The annealing temperature also seems to be an important control parameter in the modification of the shape and
size of Pt NP which can be understood by looking to the morphological changes. Here, the annealing tends to change the arrangement of the Pt NPs from film with coarse grains to the NPs with equiaxed matrix. Furthermore, it can also be seen that NPs tend to coalesce to each other and form bigger NPs rather than being equiaxed with the increase of thickness.

Figure 4 shows the dependency of the measured sheet resistance of Pt NP/graphene structure on the film thickness as a function of annealing temperature. As shown in Figure 4, the resistance increases as the annealing temperature increases, thus it could be said that the overall conductivity decreases at higher annealing temperature. This seems to be related to the decomposition of the graphene layer during the annealing (Phan & Chung 2014). It was reported that graphene matrix tends to decompose at temperature of 480°C under the pyrolytic conditions in N₂ atmosphere (Phan & Chung 2014). In this work, the annealing is performed under N₂ at annealing temperature beyond 500°C which tends to decompose the graphene matrix, where certain part of sp² bonds in graphene start to break resulting to the graphitic formation (Phan & Chung 2014). Such decomposition of graphene matrix will deteriorate the charge transport property to certain extent and hence the conductivity of the entire structure will be reduced (Ali & Hashim 2016; Phan & Chung 2014).

Moreover, the sheet resistance is found to be inversely proportional to the film thickness. Here, a 15 nm-thick Pt film on graphene shows the lowest sheet resistance as compared to the other thinner films at all annealing temperatures. This could be attributed to the generated size, shape and arrangement of the Pt NPs as shown in Figure 5. It can be seen that, at 700°C of annealing temperature, the
generated Pt NP’s grain size from 15 nm-thick film is found to be around ~130 nm in width. At the same annealing temperature of 700°C, the generated Pt NP’s grain size for 6 nm-thick film is only 25 nm in width. Even though the decomposition of graphene is enhanced with the increase of temperature, the coalescence of NPs seems to lower down the sheet resistance of Pt NP/graphene structure. In order to reduce the effect of graphene decomposition, annealing at lower temperature is desirable.

Figure 6(a), 6(b) and 6(c) shows the FESEM images of the Pt/graphene structure annealed at lower temperature of 400, 500 and 600°C, respectively. Here, the thickness of Pt film is fixed at 16 nm. The sample annealed at 600°C is the same sample shown in Figure 3. As can be seen in Figure 6(a) and 6(b), the Pt NPs phase exists in island form where the boundaries of the islands can be clearly seen (denoted by yellow lines). This could be attributed to the arrangement of Pt atoms across the graphene atomic layer. It can also be understood that the arrangement of NP in island form start to diminish with the increase of temperature where almost no boundary is observed for the sample annealed at temperature of 600°C as shown in Figure 6(c). Again, this is attributed to less decomposition of graphene atomic layer with the decrease of temperature by taking into consideration that the thermal decomposition temperature for graphene is just above 500°C as reported by Wei et al. (2015).

The cyclic response of fabricated Pt NP/graphene sensor exposed to constant hydrogen concentration (0.5% diluted H₂) at room temperature (RT) for 90 min-span is shown in Figure 7. Here, the sample deposited with 16 nm-thick Pt and annealed at 500°C is used. The measurement is done at atmospheric pressure. The exposure of the device to H₂ gas leads to the decrease of the measured current, whereas, the removal of H₂ results to the increase of measured current back to the initial value. The response and recovery behavior of the sensor is very stable where the response and the recovery times were found to be 3 s and 9 min, respectively. The cyclic response of fabricated Pt NP/graphene sensor exposed to different concentration H₂ (5, 2 and 0.5% concentration) is shown in Figure 8(a). Such measurement was conducted to investigate the effect of the change of H₂ concentration on the sensor performance. It can be seen that the sensor shows fast response at all H₂ concentrations which is below 5 s with large current change of 0.3 mA. Thus, it could be said that the sensor can detect low concentration of H₂ (as low as 0.5%) and is also capable of capturing any changes in gas concentration in bulk fluid (in the range of 0.5-5%).

Furthermore, a sensitivity plot is depicted in Figure 8(b) in order to evaluate the sensor non-linearity (i.e. the linearity error). As can be seen, there is only a non-
linearity to one side of the baseline, thus the error can be determined based on the terminal base linearity (TBL) where the total non-linearity is then the difference in Y intercept between the two points P1 and P2. Accordingly, the error of linearity was found to be 0.02 mA. Such low threshold emphasizes the ability of the sensor to respond to the change in H$_2$ concentration in the range of 0.5-5%.

The measured sensing characteristics suggest that the synthesized Pt NPs are able to act as the effective cracking catalyst to allow the absorption of H$_2$ even though the deposited thickness of 16 nm is relatively thick and the H$_2$ concentration of 0.5% is low. The obtained results are comparable with the other reported works (Ali & Hashim 2016; Phan & Chung 2014).

CONCLUSION

The annealing temperature and thickness of Pt play an important role not only in the modification of the shape, size and arrangement of Pt NPs but also in the sheet resistance of the Pt NPs/graphene structure. The resistance increases as the annealing temperature increases, which seems to be caused by the decomposition of the graphene layer during the annealing. The sheet resistance reduces with the increase of thickness at all annealing temperatures. Even though the decomposition of graphene is enhanced with the increase of temperature, the coalescence of NPs seems to lower down the sheet resistance of Pt NPs/graphene structure. Pt NPs phase exists in island form when being annealed at temperature below 500°C due to the arrangement of Pt atoms across the graphene atomic layer. The response and recovery behavior of the fabricated sensor is very stable where the sensor shows fast response at all H$_2$ concentrations which is below 5 s with large current change of 0.3 mA. The synthesized Pt NPs are able to act as the effective cracking catalyst to allow the absorption of H$_2$ even though the deposited thickness is relatively thick and the H$_2$ concentration is low.

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REFERENCES


