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Fabrication and Characterization of Hydrogen Sensors Using Graphenes Formed on the 3C-SiC Thin Films

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Abstract

This paper presents the fabrication and characterization of graphene based hydrogen sensors. Graphenes were synthesized by annealing process of Ni/3C-SiC thin film. The Ni thin film was deposited on a 3C-SiC substrate and used extracts the substrate's carbon atoms under rapid thermal annealing. Synthesized graphene transferred onto SiO_2 substrate by chemically etching of Ni in HF solution. Au electrode on the graphene shows ohmic contact and the resistance was changed with hydrogen concentration. Initial resistance of graphene was around of 360 Ω and Pd coated graphene resistance shows 27 Ω. Sensing performance of hydrogen sensors based on the graphene is improved with Pd catalyst. The response factors of graphene and Pd on graphene are 0.28 and 1.26%, respectively, at 50 ppm hydrogen concentration.

Key words: Graphene, 3C-SiC thin film, Hydrogen sensor, Transferred, Pd catalyst

Introduction

Graphene, a potential candidate, after carbon nanotubes, for use in future nanodevices, has attracted wide attention since its discovery in 2004 [1]. However, the some particular characteristics of graphene make it possible to increase the sensitivity to its ultimate limit and detect individual gas macular. First, graphene is a strictly two-dimensional material and, as such, has its whole volume exposed to surface as adsorbents, which maximizes their effect. Second, graphene is highly conductive, exhibiting metallic conductivity and, hence, low Johnson noise even in the limit of no charge carriers [2]. Third, graphene has few crystal defects, which ensure a low level of excess noise caused by their thermal switching [3]. All these features contribute to make a unique combination that maximizes the signal-to-noise ratio to a level sufficient for detecting changes in a local concentration by less than one electron charge e at room temperature. However, large-area single-layer graphenes are hard to obtain via the adhesive tape, mechanical cleavage and chemical exfoliation methods. On the other hand, the growth of epitaxial graphene (EG) possesses large single-crystalline domains with uniform thickness using silicon carbide substrates. However, this structure is difficult to transfer EG from SiC to another substrate. Thus transition metals (Cu, Ru and Ni) are employed for easily transfer onto the specific substrate.

In this work, Ni/3C-SiC structure was used for synthesis of graphene by rapid thermal annealing. After remove the Ni layer in HF for 10 min, graphene transferred onto the SiO_2 for apply to resistivity type hydrogen sensor. The hydrogen sensing characteristics are elevated the range of 10~50 ppm.

Experimental

0.1 μm solid carbon source of amorphous 3C-SiC was deposited on SiO_2 substrate by CVD at 1000 ^{o}C. Transition metal of 200 nm Ni was deposited by sputtering. Graphene synthesized on the Ni layer by annealing process under ramping speed, annealing time and cooling speed were 30 ^{o}C/s, 3 mins and 50 ^{o}C/s, respectively. Annealing temperature was kept at 1150 ^{o}C. After annealing process,

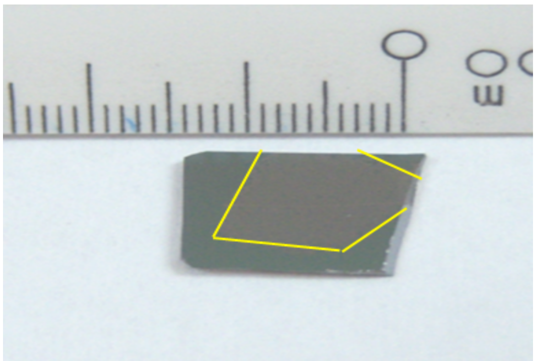


Fig. 1. Optical image of transferred graphene onto the SiO_2 substrate.

transferred onto the SiO_2 substrate. Au electrode was formed on graphene by lift-off and I-V shows the Au and graphene is ohmic contact. Pd nano particle was deposited for hydrogen catalyst metal. Chemical bonding structure, response, recovery time and response factor were evaluated. Fig 1 shows transferred bare graphene onto the SiO_2 substrate.

Results and discussion

Fig. 2 shows the Raman spectra of transferred graphene onto SiO_2. The I_G/I_D ratio was 2.73 and this value is higher than reported data [4]. D and G peaks are almost not changed with Raman measurement position. However, variation of 2D peak with each measurement position means the number of layer of graphene is different.

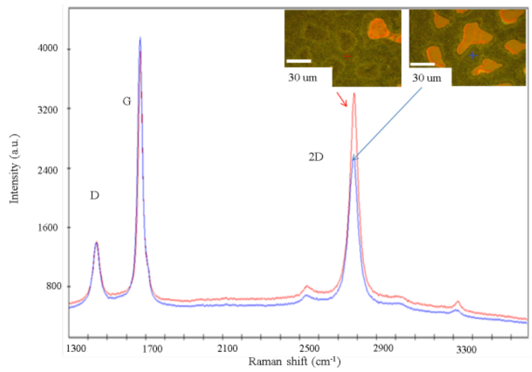


Fig. 2. Raman spectra of transferred graphene onto the SiO_2 substrate.

Fig. 3 shows TEM image of transferred graphene. 6 carbon atoms combined with each other carbons. However, it shows not symmetry structure. This means the synthesized graphene have some strain and disorder. These defects can be reducing using other transfer method.

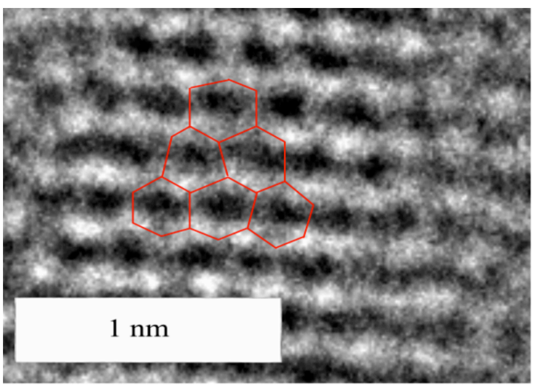


Fig. 3. TEM image of transferred graphene.

Fig. 4 shows the I-V curve of graphene and Pd doped graphene. Initial resistance of graphene was around of 360 Ω and after Pd nano particle deposition, the resistance decreased to 27 Ω. It means the Pd nano particles increased the current flow passes way.

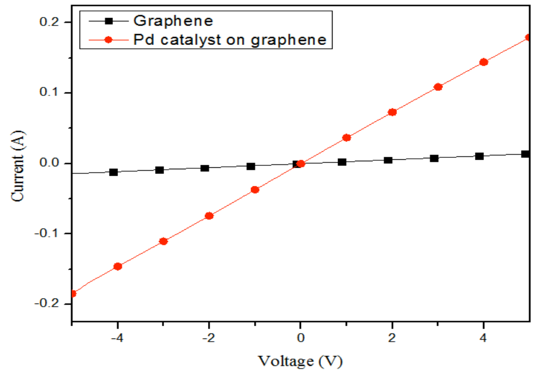
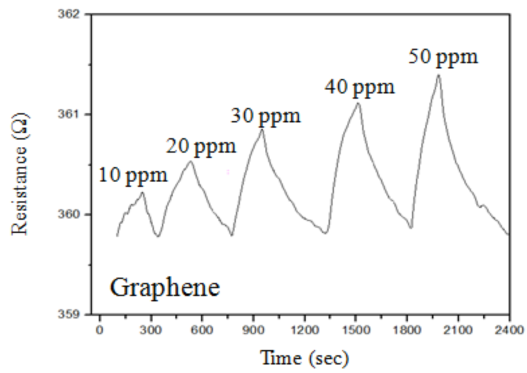
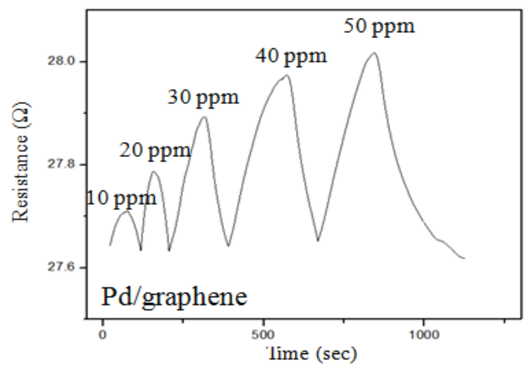


Fig. 4. I-V curve of graphene and Pd doped graphene.

The hydrogen sensing characteristics of graphene and Pd doped graphene are shown at Fig. 5 (a) and (b), respectively. The hydrogen concentration was varied in the range of 10 to 50 ppm. The resistance increased with the increase of hydrogen concentration.



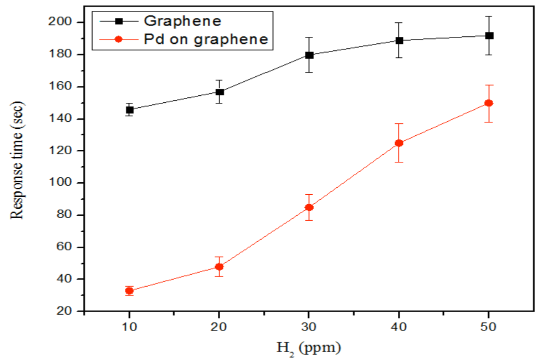
(a)



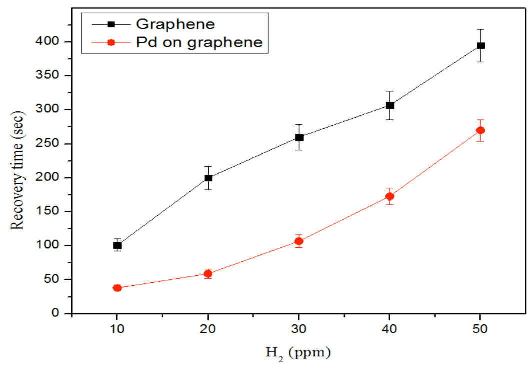
(b)

Fig. 5. Hydrogen sensing characteristics of (a) graphene and (b) Pd doped graphene.

Fig. 6 (a) and (b) shows response time (time to reach 90% of the maximum transition value) and the recovery time (time to reach 90% of the initial value) of graphene and Pd doped graphene, respectively. Response and recovery time increased with increase of hydrogen concentrations. At 50 ppm hydrogen concentration, response and recovery time of graphene was 190, 400 sec and Pd doped graphene was 140, 250 sec, respectively. Pd catalyst improved reaction of graphene and hydrogen atom. These results are more faster performance compared with reported data [5, 6].



(a)



(b)

Fig. 6. Response and recovery time of graphene and Pd doped graphene with hydrogen concentration.

Tab. 1 shows response factors of graphene and Pd doped graphene, respectively. The response factor can be considered as an indirect measurement of the device sensor signal. The response factor was calculated as follows:

$$\text{Response factor (\%)} = \left(\frac{R_{initial} - R_{response}}{R_{initial}}\right) \cdot 100$$

where $R_{initial}$ is the resistance measured in air and $R_{response}$ is the resistance at each hydrogen concentrations. Response factor of graphene was 0.28 at 50 ppm. Pd doped graphene shows the higher response factor of 1.26 at 50 ppm.

Conclusions

In this work, graphene based hydrogen sensors were fabricated and evaluated. Graphene layer was achieved by annealing of Ni/3C-SiC structure and Ni etching in HF solution. Transferred graphene shows I_G/I_D ratio of 2.73. By strain and disorder, 6 carbon atoms combine structure was not symmetry. Pd nano particle was used as catalyst and Pd doped graphene shows low resistance compared with bare graphene. 10~50 ppm hydrogen could be detected using graphene. However, response, recovery time and response factor improved using Pd catalyst. Sensors based on graphene are feasible for use in solid-state gas sensors designed for low concentration gas sensor.

Tab. 1: Response factor (%) with hydrogen concentration.

H_2 (ppm)	graphene	Pd doped graphene
10	0.13	0.26
20	0.19	0.53
30	0.25	0.76
40	0.27	0.91
50	0.28	1.26

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