Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp1234-1235

Direct Synthesis of Graphene films via Alcohol CVD for Transparent Electrode

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Abstract

We present metal-free graphene synthesis via alcohol CVD on *a*-sapphire, quartz, fused silica and silicon substrates for transparent conducting films.

1. Introduction

Graphene is expected to play a crucial role in future nanoelectronics and optoelectronics [1]. A key requirement for applications is the development of reliable, inexpensive production processes [2]. We have successfully investigated the metal-free synthesis of graphene via alcohol CVD [3]. It follows recently that the related approaches as well as van der Waals epitaxy for 2D material beyond graphene are attracting much attention [4]. In this paper, we show improved properties of graphene films directly-grown on insulators for transparent electrodes and discuss the differences on catalytic property of the substrate surface elements of aluminum and silicon. A typical photovoltaic performance of the directly-grown graphene/n-Si Schottky diodes is demonstrated.

2. Experimental

We have grown graphene films using thermal CVD with ethanol on *a*-plane sapphire, 95-nm-thick SiO_2/Si, y-cut quartz, fused silica and n-Si substrates. The pressure was kept at 0.1-10 Torr during the growth, the substrate temperature was maintained at 900-1050 ºC and argon was used as push/diluted gas at 200-400 sccm. The growth time was between 1-180 min. The source flow rate was fixed at 10 sccm. In addition, as-grown graphene films were chemically doped by $AuCl_3$ dissolved in nitromethane [5], using spin-coating. We evaluated graphene films using Raman spectroscopy with 532nm laser excitation for crystallinity and UV-VIS spectrophotometer for optical transparency. The surface morphology was analyzed by atomic force microscopy (AFM) and optical microscope. Their sheet resistances were measured mainly by van der Pauw method. The current-voltage (I-V) characteristics were measured by semiconductor parameter analyzer system.

3. Results and discussion

Figs. 1(a) and (b) show typical Raman spectra for the as-grown films and indicate graphene films due to clear 2D-band signals, respectively. It was found that basically increasing the growth temperature decreases the intensity ratio of D-band and G-band (I_D/I_G), indicating the larger domain size of graphene films. We achieve the I_D/I_G of 1.6 for on *a*-sapphire and fused silica, showing the calculated domain size of typically 11 nm. A clear domain size difference between graphene films on sapphire of Al_2O_3 and other monocrystalline and amorphous silicon dioxides SiO_2 substrates is not recognized to suggest two points: The differences on catalytic property of the substrate surface elements of aluminum and silicon is not so large. This is somewhat different from the previous results on SWNT growth on the same series of the substrates [6]. The growth mode based on Al (or Si)-C-O-H chemical system is not possibly epitaxial but also van der Waals interactive.

Figs. 2 (a) and (b) show that the relationship between sheet resistivities and the thickness of graphene films for on *a*-sapphire and SiO_2/Si, and typical optical transparency characteristics for 1.5-nm-thick grapheme on *a*-sapphire, including before/after chemical doping, respectively. The sheet resistivity dependency on the substrates used doesn`t seem to be clear, including y-quartz substrate (not shown). Here, the typical carrier mobility of 1.5-nm-thick graphene films (3-4 layers) was around 10 to 30 cm^2/Vs. Since $AuCl_3$ is a commonly used compound in conducting π-conjugated polymers, the similar doping for the graphene system is likely to be available. The chemical doping is found to make a reduction of sheet resistivity, but maintain optical transparency at 80-90%. Chemical doping for thinner films is found to be more effective and typical doped sheet resistivity is around 5 kΩ/sq for 1.5-nm-thick graphene on *a*-sapphire with a 60% reduction. Comparing with the reported sheet resistivity values [5] on catalytic CVD graphene films transferred onto SiO_2/Si, our current sheet resistivity seems to be over one order higher perhaps due to the smaller grain size.

We examined directly-grown 1-nm-thick graphene/n-Si Schottky diode. The Raman spectra of the graphene films and typical results on the current density-voltage (the evaluated barrier height: 0.69 eV) and photovoltaic (PV) performances are shown in Figs. 3 (a) and (b), respectively. The growth temperature for the device was chosen as 900ºC, relatively lower, in order to avoid carbon diffusion into Si substrate. Open-circuit voltage (V_{oc}) of 0.26 V and short-circuit current (J_{sc}) of 0.17 mA/cm^2 were improved to be 0.28 V and 0.21mA/cm^2 due to a resistivity reduction by chemical doping under Hg-Xe lamp illumination, respectively.

4. Conclusions

We have shown improved properties of metal-free graphene films directly grown by alcohol CVD. PV performance of the graphene/n-Si Schottky junction diode is also demonstrated.

Acknowledgment
The authors thank Prof. A. Kubono for fruitful discussion.

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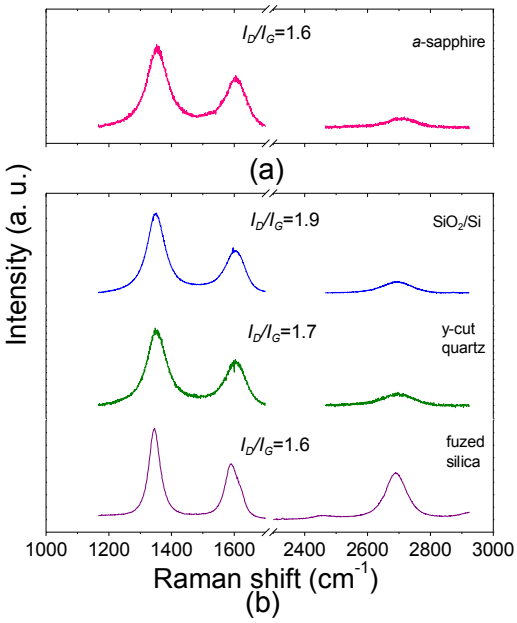
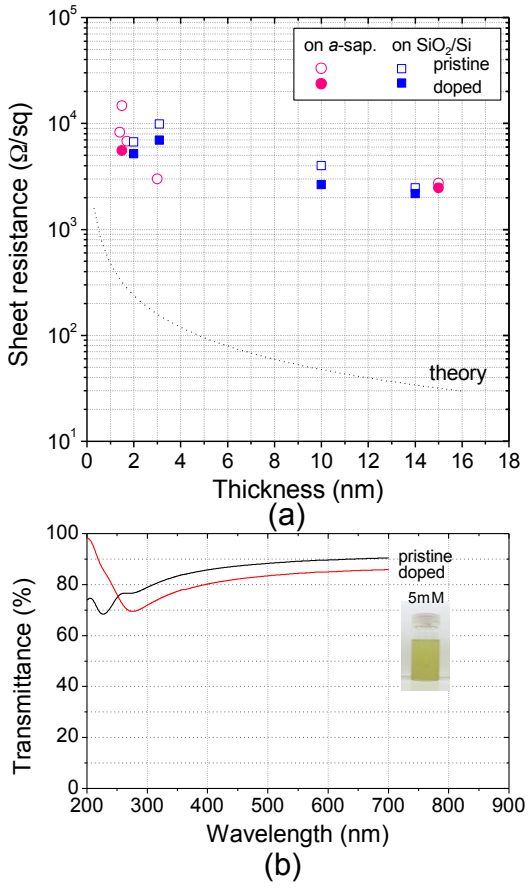
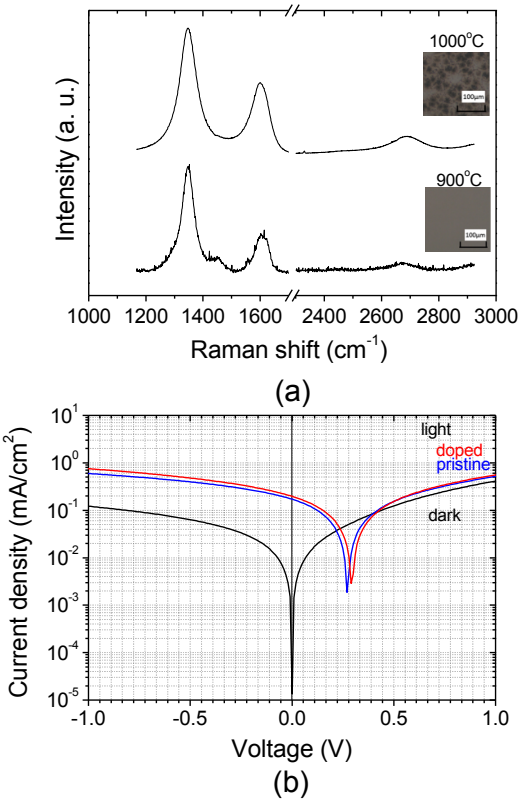


Figs. 1. Raman spectra of graphene films on *a*-sapphire (a), 95-nm-thick SiO_2/Si, y-cut quartz and fused silica substrates (b). The typical growth conditions of temperature, pressure and time, are 1040 ºC, 10 Torr, and 2 min, respectively.



Figs. 2 (a) Sheet resistances of pristine and doped graphene films on *a*-sapphire and SiO_2/Si substrates as a function of the thickness. And (b) typical transmittance performances of 1.5-nm-thick graphene on *a*-sapphire substrate for pristine and 5 mM $AuCl_3$ doped conditions.



Figs. 3. (a) Raman spectra of directly-grown graphene on n-Si substrate (native oxide:2nmt) at 1000 and 900ºC and (b) current density-voltage characteristics on the grapheme (900 ºC)/n-Si Schottky diode in dark condition, including photovoltaic performances under Hg-Xe lamp illumination for pristine and $AuCl_3$ doped conditions. Small improvements on V_{oc} and J_s are found.