ABSTRACT

This work presents a graphene-diamond-metal thin film system as ultraviolet (UV) light sensor on a flexible substrate. New scientific and engineering breakthroughs are: (1) first experimental investigation of electrical and optical properties of carbon-based sp2-sp3 (graphene-diamond) junction; (2) a peel-and-stick fabrication process to make flexible diamond thin films from CVD-grown micro crystalline diamond (MCD) wafers; and (3) a sandwich-like vertical sensor structure with graphene as a transparent top electrode, and metal (Ti-Au) as an ohmic bottom contact electrode. As such, the proposed detector/architecture can open up a new class of scheme to build diamond-based, attachable, portable and wearable optoelectronic systems.

INTRODUCTION

Diamond for Ultraviolet Photo Detection

Various wide-bandgap materials have been proposed and prototyped for ultra-violet (UV) photon detection, including diamond [1-3], ZnO [4], SiC [5], GaN [6], AlN [7], etc. Among them, diamond is an ideal candidate owing to its exceptional optical, electrical and thermal properties. First of all, its large bandgap (5.5eV) provides wide transparency window from UV to mid-infrared. Most reported diamond photodetectors have a cut-off wavelength at around 260nm. Since solar radiation on earth is longer than 280nm, diamond photodetectors can be completely solar-blind as well as making most use of the solar-free spectrum (<280nm range). The wavelength discrimination from UV to solar spectrum enables the so called Solar-Blind UV (SBUV) technology. SBUV has wide applications in both industry and military, such as corona/UV detection on electrical powerlines, manufacturing facilities, environmental and biological monitoring, muzzle flash, missile plume, and security surveillance. Furthermore, diamond is known to have high thermal stability, radiation hardness and chemical resistance which help the resilience and stability of diamond-based devices without good cooling and protection systems usually required for silicon-based detectors.

Devices based on single crystalline diamond require high cost for mass production such that systems based on various chemical-vapor-deposition (CVD) techniques have been developed to grow micro-crystalline (MCD) and nano-crystalline diamond (NCD) at the wafer scale with relatively low cost [8]. Although MCD and NCD have lower electrical, optical, mechanical and chemical qualities than their single-crystalline counterparts, photodetector devices based on MCD and NCD have been successfully demonstrated with good performances [3].

Graphene Transparent Electrode and Heterojunction

In previous works [1-3], diamond UV detectors are built with an interdigitated metal electrode structure which blocks ~50% of incident UV light. Planar electrodes also cause non-uniform electric field distribution in diamond, which reduce the effectiveness in collecting the photo-generated electron-hole pairs in the diamond films. It has been shown that graphene is 98% transparent in UV range and functions well as a transparent electrode [9]. Therefore, it is expected that the performance of a diamond photodetector could be improved by replacing the lateral, interdigitated metal electrodes with a vertical, sandwich electrode structure: uniformly-covered graphene top electrode and ohmic metal bottom electrode.

A Schottky-like heterojunction is established at the interface between graphene and a semiconductor, such as the graphene-silicon system [10, 11]. The Schottky barrier height depends on the work function of graphene, semiconductor electron affinity energy, and other possible interface states. When the Schottky-junction is reversely biased, the depletion width in the semiconductor will expand with a built-in electric field. Consequently, photo-carriers generated due to band-to-band excitation within the depletion region can be separated and swept to opposite electrodes as the drift current. Minority photo-carriers generated outside the depletion region will be driven by the carrier concentration gradient and diffused into the depletion region as the diffusion current. Furthermore, certain amount of carriers from graphene may jump across the Schottky barrier and become the internal photoemission current. The various contributions of these three components add up to become the overall photocurrent inside the heterojunction.

CONCEPT

Figure 1 shows the schematic structure of the sp2-sp3, graphene-diamond UV detector. The active layer is a 2μm-thick MCD thin film, which is sandwiched by a single-layer graphene as the top electrode to allow maximum light penetration and a bottom metal ohmic contact (Ti/Au 150nm/200nm) is grounded. The single-layer graphene has 98% transmission in UV range, as well as good conductivity (~10^2-10^3 ohm/sq.) as an electrode. The bias voltage is applied through a contact pad (SiO2/Ti/Au 50nm/5nm/50nm) deposited between the diamond and graphene.

Figure 2 illustrates the band diagram of the graphene-diamond heterojunction where E_g, E_c, E_v, qφ are the bandgap (~5.5eV), conduction band edge, valence band edge and electron affinity energy of MCD. Also, qφ_G represents
the work function of graphene (~4.5eV). Diamond’s electron affinity energy depends strongly on post processing conditions, such as annealing, with a magnitude around 0.7eV-1.45eV for annealing temperature from 500°C to 1150°C [12]. Negative electron affinity can also be induced under some conditions. An interface layer of thickness $\delta$ and potential drop $\Delta$ could be introduced and assuming $q\chi\sim0.7eV$, the final Schottky barrier height is therefore expressed as:

$$q\Phi_B=E_g-(q\Phi_G-q\chi)-q\Delta=1.7eV-q\Delta \quad (1)$$

The MCD layer is doped with boron with $N_A\sim10^{15} \text{ cm}^{-3}$. The depletion width ($W_D$) with an external bias voltage can be calculated by:

$$W_D = \frac{2\varepsilon}{qN_A} (V_{bi}-V-\frac{kT}{q}) \quad (2)$$

where $\varepsilon$ is permittivity of MCD (~5.5 $\varepsilon_0$), $V_{bi}$ is the built-in potential, $V$ is applied bias voltage. As shown in Fig. 3, the depletion width is estimated to be 0.85μm at equilibrium condition and is expanded to 1.8μm under a 5V reverse bias. This analysis is the foundation for the 2μm-thick MCD layer, which is roughly the sum of depletion and diffusion length (~0.5μm in [13]) under a typical magnitude of reverse bias. As such, photo-carriers generated both inside the depletion region and within the distance of the diffusion length outside the depletion region can be effectively collected.

**FABRICATION**

Device fabrication process is shown in Fig. 4. The MCD is grown by the Hot Filament Chemical Vapor Deposition (HFCVD). The substrate is a silicon wafer with thermally grown oxide. It is heated to 720 °C by an array of tungsten wires when a gas mixture of CH₄, H₂ and TMB (B(CH₃)₃) is introduced into the CVD chamber. After the HFCVD process, the MCD (together with the substrate) is annealed at 500°C for 45mins to enhance the crystalline structure and optical property as described in [3].

Ti/Au (150nm/200nm) is deposited by electron beam evaporation and annealed at 450°C for 45mins to form ohmic contact as the bottom electrode.

In Fig. 4(2), a double-sided tape is first is mechanically punched to have small opening holes and adhered to the diamond film. The bonding strength between the MCD and silicon substrate has been weakened due to the large thermal mismatch between the two materials. After several trial and error processes, Nitto Denko 3195 VS is chosen as the best tape as its mechanical properties (stiffness, adhesion force … etc.) match well with MCD to minimize possible damages on the diamond thin film. Experimentally, diamond films from a 4-inch wafer have been successfully peeled off without observable damages.

In Figures 4(3) and (4), the CVD-grown graphene (single layer graphene from Graphene Supermarket) is transferred onto the MCD diamond film. The assembly is then transferred and attached to a flexible polymer substrate and silver paste is used to construct conductive interconnects between the polymer substrate and the tape as illustrated. The electrical contact for the top electrode is established via a pre-patterned metal pad made of SiO₂/Ti/Au with the thickness of 50nm/5nm/50nm respectively. The graphene is originally grown a copper foil and the copper is etched away in saturated FeCl₃ solution and rinsed in deionized water, resulting in a single-layer graphene floating on top of
After dipping the device chip into the deionized water and picking up the graphene sheet on top, the transfer process is accomplished. Drying and annealing at 120°C is conducted next to minimize possible defects at the graphene-diamond interface.

Figure 4: Fabrication process: (1) Hot Filament Chemical Vapor Deposition (HFCVD) of MCD, evaporation and annealing of bottom ohmic contact. (2) The peeling process from the silicon wafer. (3) Sticking to an arbitrary, flexible substrate. (4) Graphene transfer.

RESULTS AND DISCUSSION

The transferred graphene is visible under Scanning Electron Microscopy (SEM). The boundary of the graphene sheet can be identified in Fig. 5 (a). The left part with brighter color is the bare MCD and the right part with a bit dark color is MCD with graphene on top. As expected, bare MCD shows higher brightness under SEM due to stronger electron charging effect, while graphene has lower brightness since electrons can quickly move away. In Fig. 5 (b) we notice that there are graphene micro-ripples formed in a relatively random fashion. This is expected for graphene to release film stress during the post-transfer annealing process, similar to the buckling effect in MEMS micro-bridges and cantilevers. It should be noticed that these ripples could induce interface defects and trapping of incident photons and recombination of photo-generated carriers. Further investigations are needed to improve interface quality for better efficiency.

Raman spectroscopy shown in Fig. 6 validates the successful transfer of graphene on diamond. The sample shows a strong sp³ peak at ~1332 cm⁻¹ from the 2μm diamond film, as well as G peak (1582 cm⁻¹) and 2D band (~2700 cm⁻¹), which implies the existence of the graphene. Optoelectronics performance is characterized by measuring current-voltage (I-V) curves (Fig. 7) in dark environment and under illumination. A 300W Xenon lamp is used as the light source. The broadband radiation from Xenon lamp covers the wide spectrum range from UVC to NIR. Single-wavelength light is obtained by filtering the Xenon lamp’s broadband radiation using a monochromator installed with a holographic grating. Optical power density is calibrated by a commercial silicon photodetector. The prototype device has an active area of ~0.87 cm².

Figure 5: SEM pictures of graphene transferred onto MCD: (a) boundary of the transferred graphene on the right side, and (b) graphene ripples observed at high magnification.

Figure 6: Raman spectroscopy of graphene-on-diamond material system.

Under the dark environment, the photodetector shows a typical rectifying I-V curve (black curve in Fig. 7). When the junction is reversely biased, higher potential is applied at the top graphene electrode. Experimentally, it is observed that under forward bias at V=−5V, the output current is 6μA while under reverse bias at V=5V, the output current is 140nA. The ideality factor and barrier height are two critical parameters in characterizing the Schottky junction and can be extracted from the forward bias I-V data as shown in Fig. 8 by the models proposed in [14]. It is found that the ideality factor remains around unity when the forward bias voltage is small, indicating an ideal thermionic emission and it increases significantly (almost linearly) with respect to the bias voltage, probably due to the increasing quantum tunneling effect through the Schottky barrier. On the other hand, the zero-bias barrier height is 1.57eV which is reasonably close to the estimation (Eq. (1)) based on the band diagram. The barrier height gradually drops under the forward bias due to the image-force lowering effect, as commonly observed in other Schottky diodes.

Under the UV illumination at 220nm (the blue curve in Fig. 7), significant increase in photocurrent can be observed. As expected, photocurrent under the reverse bias is much larger than that under the forward bias because the depletion region where most photo-carriers can be effectively collected is enlarged under the reverse bias.
CONCLUSION

Thin film photodetector based on the graphene-on-diamond (carbon sp²-sp³) heterojunction is fabricated and tested for application in solar-blind UV detectors. A novel "peel-and-stick" method is demonstrated in order to make ultrathin microcrystalline diamond films and graphene is transferred and attached to the back and smooth side of the diamond films. I-V curves of the graphene-diamond photodetectors have been characterized under various environments, including dark, UVC illumination and visible light, respectively (Fig. 7).

The demonstrated devices could find promising application in highly-sensitive solar-blind UV detectors. Further improvement on the interface between graphene and diamond could lead to even higher optical responsivity.

ACKNOWLEDGEMENTS

The authors greatly appreciate help from Miss Sarah Brittmann and Miss Fan Cui. The device is fabricated in the UC Berkeley Marvel Nanofabrication Laboratory. The project is supported in part by Siemens Inc.

REFERENCES


CONTACT

*Kaiyuan Yao: kyyao@berkeley.edu