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Comprehensive Investigation of Single Crystal Diamond Deep-Ultraviolet Detectors

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The wide bandgap of diamond, along with its extreme semiconductor properties, offers the promising route for deep-ultraviolet (DUV) detection, especially under solar-blind condition and harsh environments. The ideal photodetector should generally satisfy the 5S requirements such as high sensitivity, high signal-to-noise ratio, high spectral selectivity, high speed, and high stability. In this paper, we comprehensively investigate the DUV detectors fabricated from various kinds of single crystal diamonds such as boron-doped diamond homoeptaxial layer, intrinsic diamond homoeptaxial layers with different thicknesses, and single crystal diamond substrates. The post process such as hydrogen plasma treatment on the performance of the DUV detectors is also examined. The strategies to develop high-performance diamond DUV detectors are provided.

1. Introduction

Deep ultraviolet (DUV: 350–190 nm) detectors can find various applications ranging from environment security, information technology, medical treatment, astronomical observation, and military application to inter-satellite communications.1,2 Although III–nitrides are promising candidates for DUV detection, the defects greatly degrade the performance.3,4 Diamond with a wide bandgap of 5.5 eV, along with the extreme properties such as a high thermal conductivity, high carrier saturation velocity and mobility, offers the highest figure-of-merit for high-performance DUV detectors meeting the requirements of high sensitivity, high signal-to-noise ratio, high spectral selectivity, high speed, and high stability (we called 5S). However, it is difficult to utilize polycrystalline diamond for achieving the 5S requirements due to the existence of grain boundaries and non-diamond impurities.3) These defects greatly affect the photoresponse, leading to strong persistent photoconductivity (PPC) and sub-bandgap response in the visible light region.6–12 Therefore, single crystal diamond is highly desirable to eventually satisfy the 5S requirements.

We have been making efforts in improving the performance of diamond DUV detectors by designing various device geometries.13–16) The reported devices include interdigitated-finger metal–semiconductor–metal (IDF-MSM) photoconductor, MSM photodiode, conventional Schottky photodiode (SPD), and interdigitated-finger Schottky photodiode (IDF-SPD). Our previous work was based on the lightly boron-doped diamond thin films grown on the type-Ib diamond substrates. In such a case, a sub-bandgap response at around 270 nm was always observed due to the thin film nature of the epitaxial layer. In this paper, comprehensive study is made on the photodetectors fabricated from single crystal diamonds with various thicknesses, different impurity natures, and post processing, in order to clarify the route to develop high-performance diamond DUV photodetectors and to understand the origin of the sub-bandgap photoresponse.

2. Experimental Procedure

2.1 Diamond thin films growth

Photodetectors were fabricated on different homoeptaxial diamonds, which include intrinsic diamond thin films with varied thicknesses and boron-doped diamond epilayers grown on type-Ib (100) diamond substrates. Devices were also directly fabricated on type Ib and IIa diamond substrates.

Two types of microwave plasma-enhanced chemical vapor deposition (MPCVD) systems were utilized for the growth of the homoeptaxial diamond layers. For the boron-doped diamond growth, the concentration of the CH4 source was as low as 0.08% diluted with H2. Boron doping was performed using trimethylboron [B(CH3)3, TMB] as the source gas. The growth parameters were as follows: a total gas pressure of 80 Torr, a H2 gas flow rate of 500 sccm, and substrate temperatures of 900–960 °C. The boron-doped samples were deposited at the TMB/CH4 ratios of 2.5–100 ppm. The film thicknesses had boron concentrations from 1015–1020 cm–3. The film thickness was about 0.5 μm.

The intrinsic diamond epilayers were grown in the experimental MPCVD setups which have never been utilized for intentional impurities doping. The concentration of the CH4 source to H2 was varied from 0.1 to 10%. The other growth parameters were as follows: a total gas pressure of 80–120 Torr, H2 gas flow rates of 100–500 sccm, and substrate temperatures of 930–1050 °C. The film thickness was varied from 0.2 to 80 μm.

The as-fabricated diamond surface was basically hydrogen-terminated and an oxidation treatment of the epilayers using boiled acid solution of H2SO4 and HNO3 led to oxygen-terminated surface.

2.2 Devices design and fabrication

A standard photolithographic technique was used for the devices fabrication. The Schottky photodiodes were fabricated on the boron-doped diamond epilayer. The metal contacts were deposited by using a Biemtron RF-magnetron sputter apparatus at a base pressure of 10–7 Pa. The deposits were conducted under argon atmosphere at room temperature at an input RF power of 100 W and argon pressure of 1 Pa.

Titanium (Ti) covered by tungsten carbide (WC) was used as the Ohmic contact, formed by annealing at 600 °C for 1 h. A nominally stoichiometric WC disk with 99% in purity and 25 mm in diameter was used as the target. The device structures studied in this paper are illustrated in Fig. 1. The conventional SPD device is a concentric type based on an
inner semitransparent Schottky circle with a diameter of 400 μm. The interspacing between the Schottky and the surrounding Ohmic contacts was 20 μm. The MSM and IDF-SPD devices are characterized by a finger spacing and device active area of 10 μm and 52 × 10⁻³ mm², respectively.

2.3 Device characterization
The electrical/photoelectrical measurements were carried out in air by a two-probe method. The spectral response was measured in the range of 210 to 630 nm by using a 500 W Xenon lamp. The incident light power was calibrated by a UV-enhanced Si photodiode. In particular, the responsivity was unified at the light of 220 nm illumination if there is no additional mention. The power intensity of the 220 nm light illuminated on the photodetectors was estimated to be around 10–20 μW/cm². The spectral response was measured by DC technique for the devices with low dark current and fast response speed or by a lock-in amplifier technique with a chopped frequency of 100 Hz. The time response was measured by mechanically switching on/off or chopping the above band gap illumination at 100 Hz.

3. Results and Discussion
3.1 Photodetectors fabricated on boron-doped diamond
Various photodetectors such as Schottky photodiodes, back-to-back MSM photodiodes, and photoconductors were developed on the boron-doped diamond thin films grown on the type-Ib diamond substrates. Boron in the epilayer and nitrogen in the substrate provided the base for tailoring the overall performance of the diamond DUV photodetector. Due to the nitrogen defect in the substrate, holes in the boron doped epilayer will be depleted. Calculation showed that if the boron content was lower than 10¹⁵ cm⁻³, all the holes were depleted for the epilayer with a thickness of 500 nm. Therefore, even for MSM photoconductor with annealed Ti/WC contacts, the dark current could be extremely low (<0.1 pA). Due to the electron trapping effect by the nitrogen defect in the type-Ib substrate, the DUV sensitivity was enhanced greatly with a gain more than 10⁴ or a quantum efficiency of 10⁶. Such an enhanced DUV sensitivity was partially attributed to the “recovery” of the holes in the epilayer. At the same time, the electron generated in the substrate can recombine with the holes in the epilayer, allowing the possibility of fast response speed. However, if the boron concentration in the homoepitaxial layer is too high, strong PPC appears.

Based on the unique nature of the wide-bandgap of diamond, the high barrier interface of the metal/diamond contacts for electrons blocks most of the photo-generated electrons from the substrate nitrogen. Therefore, the spectral response with high DUV/visible light rejection ratio could be obtained as high as 10⁶ even for a thin homoepitaxial diamond layer of 500 nm. The photoresponse properties of the DUV photodetectors (SPD, IDF-MSM, IDF-MSM) based on boron-doped diamond epilayer with a thickness around 500 nm are summarized in Table I. The 5S performance except the stability can be revealed from this Table. The conventional SPD shows relatively poor performance. The IDF-MSM and IDF-SPD revealed a high performance such as low leakage current (<0.1 pA, high signal-to-noise ratio), high quantum efficiency (sensitivity) of 10⁶ at 220 nm light, a DUV/visible light rejection ration (spectral selectivity) of 10⁵, and a fast response (speed) smaller than 0.3 s. No degradation was observed for these detectors after several hours irradiation even by strong excimer DUV laser, suggesting a good stability.

Although high-performance diamond photodetectors were achieved by properly designing the device configuration, there exist several points to be addressed. An obvious feature is the appearance of the sub-bandgap of 260–270 nm photoresponse regardless of the device configuration, as shown in Fig. 2. Another point is the photoresponse located at around 550 nm, which sometimes was observed in thick diamond epilayers.18,19

3.2 MSM photodetectors fabricated on intrinsic homoepitaxial diamond layers
To improve the spectral response or understand the origin of the sub-bandgap photoresponse, intrinsic diamond epilayers with various thicknesses grown on type-Ib diamond substrates were utilized for DUV detectors. The intrinsic diamond here means homoepitaxial diamond layers grown on type Ib-diamond substrates in the MPCVD setup, which has never been used for the purpose of impurities doping. Therefore, it is believed that boron cooperation can be ignored in these epilayers. The diamond surface was oxidized by boiling in a mixture solution of HNO₃ and...
Due to the high resistivity of the epilayers, all the photodetectors fabricated on the intrinsic diamond epilayers exhibited extremely low dark current (<0.1 pA) up to 32 V at least. Figure 3 presents the current–voltage (I–V) characteristics under above band gap illumination (220 nm) of the MSM photodetectors fabricated on the diamond epilayers with different thicknesses. The I–V characteristics show nearly linear behavior for the film with a thickness of 100 nm, which suggests that the bulk rather than the metal/diamond interface dominates the photoconductivity. The responsivity at 32 V was calculated to be about 7 A/W, corresponding to a quantum efficiency of 0.38%. As expected, the DUV responsivity increases with the film thickness due to the reduction of the bulk resistance and more effective optical absorption. The responsivity at 220 nm light increases to 0.041 A/W with a corresponding quantum efficiency of 23% at 32 V for the film with a thickness of around 200 nm. As the epilayer thickness increases to be around 5 µm, the responsivity at 220 nm light reached 1 A/W, displaying an obvious photoconductivity gain with a value around 6 (or quantum efficiency 600%). In Fig. 4, the dependence of the responsivity at 220 nm light illumination for an applied bias of 32 V versus the epilayer thickness is illustrated. The I–V characteristics of the thicker film display a nonlinear behavior, different from the thinner ones. Numerical fittings revealed that the electrical transport of the photo-generated carries was governed by the metal/diamond interface. At low DUV intensity (i.e., 1.3 µW/cm²), the electrical transport follows thermionic-field emission tunneling process. At high DUV intensity (i.e.,...
20 \mu W/cm^2), field-emission tunneling determined the electrical transport process. The carriers injection produced the photocurrent gain. The origin for the carriers injection was attributed to the trapped charges at the metal/diamond interface, which was generated by DUV light illumination.\cite{16,20} We note that such kind of traps should not depend on the film thickness.

We also studied the photoresponse from the homoepitaxial diamond layer with a thickness of 80 \mu m. However, we found that the responsivity decreased without observing the photocurrent gain. At this moment, the origin of the decrease in the photocurrent for the thicker epilayer is not clear. One possible reason is that as the homoepitaxial layer becomes thicker, some defects also grow up. These defects act as the recombination centers, lowering the photoresponsivity. Actually, the penetration depth of the 220 nm light in diamond is around 10 \mu m.\cite{21}

It should be noted that the detectors without gain do not reveal clear PPC. While for the film with a thickness around 5 \mu m, only a little PPC was observed due to the meal/diamond interface trapping effect. This is consistent with our previous results that the photocurrent was always accompanied by PPC.

The spectral response of the film with different thicknesses was investigated, as shown in Fig. 5, which was normalized by the incident power density. The sharp band-edge response is clearly seen. All of the plots showed the highest sensitivity at 210 nm. The shoulder at around 270 nm appears as previously observed for the thin diamond epilayers. Visible light response at 450–600 nm was also observed. As the films became thicker, the 270 nm photoresponse turns to be less distinct and finally disappears. Since the 240 nm light response is close to the free-exciton emission wavelength of diamond, we plot the responsivity ratio of the 210 nm to the 240 nm light in Fig. 6. This ratio can reflect the DUV photocurrent from the epilayer. Therefore, the 210/240 nm light response ratio suggests that the nitrogen in the substrate plays a weak role in the photoresponse for a thick intrinsic film. The spectral response investigation excludes the substrate nitrogen as the main factor for the gain. On the other hand, it is disclosed that the visible light absorption occurs from 630 to 450 nm for all the intrinsic epilayers. For the thin epilayer, the visible light response most likely originates from the substrate, in which the photoresponse forms into a band from 630–450 nm. Instead, the visible light response at 270 nm is likely originated from holes, since the photocurrent gain can also be observed.

![Fig. 5. (Color online) Spectral response of the MSM detectors fabricated on the intrinsic homoepitaxial layers grown on the type-Ib diamond substrates with different thicknesses.](image1)

![Fig. 6. (Color online) The responsivity rejection ratio of the 220/240 nm light of the MSM detectors fabricated on the intrinsic homoepitaxial layer grown on the type-Ib diamond substrates with different thickness.](image2)

![Fig. 7. (Color online) The photocurrent–voltage characteristics at 220 and 630 nm light illumination of the MSM photodetectors fabricated on the intrinsic homoepitaxial layer grown on the type-Ib diamond substrates with a thickness of 80 \mu m.](image3)
3.3 Photoresponse from single crystal diamond substrates

3.3.1 Photoresponse from oxygen- and hydrogen-terminated type Ib diamond

For comparison, HPHT type-Ib and IIa diamond were also employed for the fabrication of MSM-type photodetectors with Ti/WC contacts. The type-Ib diamond is well-known to contain a large amount of nitrogen. DUV photocurrent of the MSM devices fabricated from the type-Ib diamond substrate with oxidized surface is always low. The typical quantum efficiency is in the order of 0.1%. Annealing the Ti/WC contacts at 600°C for 1 h did not improve the DUV responsivity. The spectral response from the type-Ib diamond revealed a poor selectivity between DUV light and visible light.

The DUV photocurrent can be enhanced by five orders of magnitude after hydrogen plasma treatment of the Ib diamond substrate, as displayed in Fig. 8. Photocurrent gain as high as 100 or more could be achieved for the MSM devices with as-deposited WC Schottky contacts. The dark current of the hydrogen-terminated diamond detectors can be tailored by controlling the hydrogen plasma treatment process. The response speed can be varied from second to hundred seconds depending on the hydrogen treatment. The ozone treatment can also reduce the dark current or increase the response speed of the hydrogen-terminated diamond photodetector. In addition, the spectral response was also greatly improved after hydrogen terminating. The 210 nm/visible light ratio was improved to be as high as 10^5, shown in Fig. 9. The shape of the spectral response is quite similar to those of thin homoepitaxial diamond layers grown on the type-Ib diamond substrates, with the appearance of the 270 nm shoulder. The origin of the photocurrent gain from the hydrogen-terminated diamond detectors is similar to that of boron-doped diamond photodiode operated at forward bias. Hydrogen termination of diamond is well-known to produce the two-dimensional holes conductivity on the surface. These holes are depleted by the nitrogen in the substrate, leading to a low dark current. Upon DUV light illumination, photo-generated electrons are trapped by the nitrogen, partially recovering the holes in the surface layer caused by hydrogen termination. On the other hand, electrons generated from the nitrogen defect recombine with the holes on the surface, which enhances the response speed. Since the plasma treatment is quite simple, it provides an alternative strategy to develop high-performance diamond DUV photodetectors. We mention that the detector stability strongly depends on the ambient atmosphere due to the hydrogen termination.

3.3.2 Photoresponse from oxygen-terminated type IIa diamond

MSM devices with as-deposited WC contacts were also made from the homoepitaxial layer deposited on the commercial type-IIa substrates (containing little nitrogen). The IIa diamond detectors displayed much higher DUV photoresponsivity than those of fabricated from the type-Ib diamond substrates, as shown in Fig. 10. Basically, no dark current can be detected by our picoampermeter (resolution: <0.1 pA) from the IIa diamond. The responsivity at 220 nm light is calculated to be 0.49 A/W at 30 V, corresponding to a gain close to 3. The photocurrent gain mechanism is mostly originated from the shrinkage of the barrier at the metal/diamond interface, as described previously. Photo-detectors fabricated from the IIa diamond also exhibit fast response speed.
response and the signal can be easily detected by the oscilloscope, as disclosed in Fig. 11. The spectral response from the IIa diamond in Fig. 12 clearly reveals the band-edge absorption, without the appearance of the 270 nm shoulder. However, visible light response can still be observed, which strongly depends on the quality of the IIa diamond.

4. Conclusions

Various single crystal diamonds were utilized to fabricated DUV diamond photodetectors with Schottky photodiode and MSM device configurations. The overall performance such as sensitivity, signal-to-noise ratio, spectral selectivity, speed, and stability were investigated in these diamond DUV detectors. The results were summarized in Table I. There is a balance among the DUV responsivity, response speed, and spectral response. The thick intrinsic diamond layer with the thickness larger than 5 μm and the type IIa diamond substrate exhibited high DUV responsivity with photocurrent gain; while the response speed kept relatively fast. Relatively high responsivity can also be achieved on the photodetectors fabricated from the p-diamond epilayer on the type-Ib diamond substrate or on the hydrogen-terminated Ib diamond substrate. The response speed can be fast if the boron-doping level is properly controlled. The thinner diamond layers (<1 μm) always showed the 270 nm photoresponse regardless of the device configuration. The spectral response in the UV region was improved when the thick intrinsic diamond epilayer and the IIa diamond substrate were utilized. The 270 nm photoresponse was confirmed to originate from the type-Ib diamond substrate. Two main origins were responsible for the photocurrent gain mechanism: space charge separation and photo-generated carriers injection through the metal/diamond interface.

![Fig. 11. Transient response at 220 nm light with a power intensity of 20 μW/cm² of the MSM photodetectors fabricated on the type-IIa diamond substrate. The frequency of the chopped light is 100 Hz. The photocurrent clearly follows the reference signal.](image1)

![Fig. 12. Spectral response of the MSM photodetectors fabricated on the type-IIa diamond substrate.](image2)

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