Progress in semiconductor diamond photodetectors and MEMS sensors

Meiyong Liao
Research Center for Functional Materials, National Institute for Material Science, Tsukuba, Ibaraki, Japan

ABSTRACT
Diamond with an ultra-wide bandgap shows intrinsic performance that is extraordinarily superior to those of the currently available wide-bandgap semiconductors for deep-ultraviolet (DUV) photoelectronics and microelectromechanical systems (MEMS). The wide-bandgap energy of diamond offers the intrinsic advantage for solar-blind detection of DUV light. The recent progress in high-quality single-crystal diamond growth, doping, and devices design have led to the development of solar-blind DUV detectors satisfying the requirement of high sensitivity, high Signal-to-Noise ratio, high spectral Selectivity, high Speed, and high Stability. On the other hand, the outstanding mechanical hardness, chemical inertness, and intrinsic low mechanical loss of diamond enable the development of MEMS sensors with boosted sensitivity and robustness. The micromachining technologies for diamond developed in these years have opened the avenue for the fabrication of high-quality single-crystal diamond mechanical resonators. In this review, we report on the recent progress in diamond DUV detectors and MEMS sensors, which includes the device principles, design, fabrication, micromachining of diamond, and devices physics. The potential applications of these sensors and a perspective are also described.

1. Introduction
Diamond is an element semiconductor material owning numerous extraordinary properties such as the highest mechanical hardness in nature and the highest thermal conductivity among all the known semiconductors. By virtue of the extreme hardness, diamonds are widely used as abrasive materials in industry, such as grinding tools, blades and for cutting, drilling, and polishing, etc [1–5]. In addition to the outstanding mechanical properties, diamond also has the highest figure-of-merits for semiconducting devices due to its extraordinary properties such as the ultra-wide bandgap (UWBG) energy, the highest thermal conductivity (22 W/mm K), high carriers mobilities, large breakdown electric field (exceeding 10 MV/cm), high chemical inertness, and thermal stability [6–9].

The strategies toward large single-crystal diamonds (SCDs) include the high pressure and high temperature (HPHT) synthesis, chemical vapor deposition (CVD) on the HPHT or CVD SCD substrates, and heteroepitaxial CVD growth of diamond on iridium layer. The invention of microwave plasma CVD (MPCVD) and hot filament CVD (HFCVD) [10,11] have provided controlable growth of diamons on various substrates. The mosaic method by CVD on cloned SCD substrates opens the possibility for inch-size SCD wafers. Especially, the MPCVD growth technique has been widely used nowadays for the growth of large-size SCD [12,13] and led to numerous applications of diamond as a semiconductor material. These applications include field-effect transistors and diodes for power electronics [14–20], microwave devices [21–25], deep-ultraviolet (DUV) light emitting diodes (LED) [26–28], DUV photodetectors [29,30], radiation detectors [31–35], microelectromechanical systems (MEMS) [36–39], and quantum sensors [40–42]. The utilization of diamond as a heat sink has also been attracting growing interesting in the application of high-power high-frequency communication, electrical power switch and others, in which the thermal dissipation is a problem [43–47]. Although great progress has been made in semiconductor diamond, diamond electronics is far from reality due to several bottlenecks such as the growth of large-area low-dislocation density SCD wafers, lack of shallow dopants, and poor interface between diamond and insulators in power electronics.

In contrast to diamond electronics, diamond as DUV or radiation detectors are more developed since shallow dopants are not prerequisite and simple device structure can be adopted. The utilization of diamond as DUV detector has the intrinsic merit of solar blindness (wavelength <280 nm) due to the large bandgap energy of 5.5 eV. Therefore, an ideal diamond DUV detector shows...
no or weak response to the light with wavelength longer than 280 nm on the earth. Traditional UV-enhanced Si photodetector has intrinsic limitations in UV detection owing to its narrow bandgap energy of 1.1 eV. For other wide bandgap semiconductors such as GaN and SiC, the bandgaps are not high enough to reach the solar blindness. When using these semiconductors for DUV detection, filters are needed to reduce the background noise from the solar light. The large bandgap energy of diamond also offers the advantage of extremely low dark current. Compared to other UWBG semiconductors such as Ga_{2}O_{3}, diamond is expected to show much stronger radiation hardness upon high-power DUV illumination due to the single element nature and strong chemical carbon-carbon bonds.

Another promising application of diamond is microelectromechanical system (MEMS), which is at the rising stage since Howe developed polysilicon surface micromachining technology [48]. MEMS adds diversities to the modern electronics with high flexibility and has been a key technology of Moore [49,50]. The mature CMOS technology and deep etching of silicon have brought numerous applications of MEMS in our daily life and industry. These products include mass sensor, pressure sensor, accelerometer, gyroscope, linear or rotatory displacement sensor, microphone, optical switch, micro mirrors and radio-frequency switch, to name a few [51–55]. By virtue of the outstanding physical properties such as the highest Young’s modulus, the highest hardness, the highest thermal conductivity, erosion robustness, and the ultra-wide bandgap energy, diamond presents as a superior material for MEMS applications with high reliability and high performance superior to other semiconductors, such as low mechanical energy dissipation toward high-quality factor and high-sensitivity for MEMS sensors.

In this review, the state-of-the-art of diamond DUV photodetectors and MEMS sensors will be presented. The potential applications and a perspective of these sensors are also discussed.

2. Diamond deep-ultraviolet detectors

The principle of diamond DUV detector is based on the electrical conductivity change when light is absorbed by it to generate free electron-hole pairs across the bandgap. The photoconductive behavior of diamond was reported as early as 1934 [56]. However, until 1990s, extensive investigation in diamond photodetectors has been conducted, which was firstly on polycrystalline diamonds [57–59]. To evaluate the performance of a photodetector, one can use the 5S requirement of Sensitivity, high Signal-to-Noise ratio, high spectral Selectivity, high Speed, and high Stability [60,61]. Up to now, only SCD can satisfy the above 5S requirement for DUV detection, which is the focus of this review.

2.1. Figure-of-merits of photodetectors

The figure-of-merits of a photodetector include the follows corresponding to the 5S requirement besides the stability.

Quantum efficiency: Quantum efficiency (η) is the number of free carriers generated by one photon.

Responsivity or sensitivity: Responsivity, R_{p}, is characterized by the output signal per radiant power, P, in watts (W). Usually, the photocurrent, I_{p} (A), is the measured. R_{p} is then described as [58]

\[ R_{p} = \frac{I_{p}}{P} \]

where \( \lambda \) is the light wavelength. As a general, one can add gain, g, in the expression as

\[ R_{\lambda} = \eta \cdot \frac{\lambda}{g} \]

Spectral selectivity: The spectral selectivity is the response of a photodetector as a variation of the light with different wavelengths.

Dark current: Dark current is the electrical current measured without light illumination.

Response time: There are rise time (T_{r}), which is defined as the output level changing from 10% to 90% of the peak and fall time (T_{f}), which is defined as the output level decreasing from 90% to 10% of the peak.

Noise equivalent power: Noise equivalent power (NEP) determines the detector sensitivity with a unit of A/\sqrt{Hz} or V/\sqrt{Hz}. NEP is defined as the noise spectral density divided by the responsivity.

Specific detectivity: The specific detectivity (D') is the reciprocal of NEP normalized per square root of the sensor’s area and frequency bandwidth.

2.2. Effect of device structures

The photoresponse properties can be tailored through device designing [58]. The simplest structure is metal-semiconductor-metal (MSM) type, in which the electrical contacts can be either Schottky or Ohmic type, usually with interdigitated-finger arrangement. In most cases, symmetrical electrodes are used and there is no detected photocurrent at zero bias. The Schottky MSM photodetector has the merits of low dark current due to the metal/semiconductor barrier height and high response speed. The theoretical quantum efficiency of Schottky MSM detector is less than unity [62]. A MSM photococonductor has two Ohmic contacts, which can have external quantum efficiency much larger unity. The weakness of the MSM structure is the exposed optical receiving area to air, which may suffer from pollutants.
and surface effect. Junction devices like the Schottky photodiode (SPD) and pn- or pin-junction photodiodes [63–65] can avoid the surface effect and be operated at zero bias like a solar cell. For the SPD, the Schottky contact is usually semi-transparent, partially absorbing the incident light. The pn-junction photodiode has much higher responsivity than SPD. The above four devices structures are all reported on SCDs. However, few reports on the phototransistor structure have been found on SCDs. Besides, hetero-structured photodetectors were also reported to broaden the spectral response.

2.2.1. MSM photodetectors

A preliminary MSM photodetector based on a 20 µm thick SCD layer on type-Ib SCD substrate was reported with Ti contact [66]. The device had an equivalent noise power <1 pW. The photocurrent rejection ratio between the 220 nm to 280 nm light, was around 10^4. By properly designing the device structures, a thin film SCD layer is able to achieve high responsivity and solar/visible blind ratio. By using the surface pn-junction between the epilayer and the type-Ib substrate containing nitrogen, the holes in the epilayer can be depleted without any external bias. Therefore, the overall photoresponse properties of the SCD detector such as the dark current, responsivity, the solar/visible-blind ratio, and response speed can be modulated through boron doping. A planar interdigitated-finger type MSM photodiode fabricated from a submicron thick SCD epilayer with oxygen-terminated surface grown on a type-Ib HPHT diamond substrate was reported [67]. The device contacts are composed of interdigital-finger (IDF)-type Ti/WC electrodes, as illustrated in Figure 1(a). The as-fabricated device behaved as a photodiode (PD) with Schottky contacts due to the Femi level pinning of the oxygen-terminated diamond surface. The Schottky barrier height was from 1.2 to 2.1 eV [68]. The MSM PD turned to be a photoconductor after annealing at 600 °C for 30 min. The dark current of the MSM-PD was as low as 0.1 pA and increased to be only ~1 pA even at a bias of 20 V. Upon 220 nm DUV light illumination, marked difference in the current-voltage (I-V) characteristics was observed for the MSM-PD and photoconductor, as revealed in Figure 1(b).

For the MSM-PD, no photoconductivity, the quantum efficiency was <1 without gain. In contrast, the MSM photoconductor using the same Ti/WC contact exhibited much larger photocurrent than the photodiode. A responsivity as high as 6 A/W at 220 nm was obtained at 3 V, corresponding to a gain of 33. From the photocurrent, one could obtain the mobility-lifetime product, which was around 10^{-5} cm^2 V^{-1}. The highest responsivity was achieved at 210 nm, as seen in the spectral response in Figure 1(c). A shoulder at around 270 nm also appeared, which is due to nitrogen in the type-Ib substrate effect [69]. The discrimination ratio between the 210 nm and the visible light (400 nm) was nearly 10^8 for the photoconductor. The photoresponse at the wavelength larger than 500 nm was related to boron or nitrogen.

It should be noted that both the MSM PD and photoconductor showed fast optical switching speed. Figure 1(d) shows the time response upon the 220 nm light (intensity ~20 µW/cm²) illumination by mechanically switching on/off the optical shutter. The rising and
falling times were beyond the measurement system time constant of 0.3 s, despite the slow component during the decay. The diamond photodetector was successfully utilized to monitor the high-power DUV (193 nm) excimer laser with a pulse width around 10 ns.

### 2.2.2. Schottky photodiode

Generally, the SPD contains a semi-transparent Schottky contact and an Ohmic contact, named conventional SPD (CSPD) here [58,70]. By using the lightly boron-doped ([B]:10^16cm^-3) SCD epilayer (oxygen-terminated surface) on the type-Ib diamond substrate, the diamond SPD was fabricated by using Ti/tungsten carbide (WC) as the Ohmic contact and semi-transparent WC as the Schottky contact [71], as shown in Figure 2(a). The Schottky contact had a diameter of 400 μm. The as-fabricated diamond CSPD showed typical rectifying properties with a rectification ratio of 10^8 at ±5 V in dark condition, as shown in Figure 2(b). The ideality factor (n) and the Schottky barrier height (qΦ_B) evaluated by the thermionic emission theory [63] based on the experimental I-V curve were 1.67 and 1.59 eV, respectively, for the as-fabricated SPD. The WC Schottky contact showed thermal stability up to 500 °C even after annealing for 5 h. The dark current remained <0.1 pA, and the qΦ_B was >1 eV, and the n value became ~1 after annealing.

The as-fabricated SPD had a low photoresponsivity at 220 nm light, which saturated at reverse biases, as plotted in Figure 2(c). The saturation photocurrent, I_ph, was approximately 10^-10 A at 220 nm illumination with an intensity ~ 20 μW/cm^2. The quantum efficiency η of the as-fabricated SPD was as small as 2% (assuming g = 1) and the maximum responsivity at 220 nm light R was as low as 4 mA/W. A substantial enhancement of the photocurrent was observed after annealing for 2 h or longer. The saturation photocurrent was enhanced by 10^3 with gain compared with the as-fabricated photodiode. After annealing for more than 2 h, PPC was clearly observed, as shown in Figure 2(d).

The PPC effect can be avoided by using the photovoltaic mode of the CSPD [72], although the responsivity was as low as 0.5 mA/W at 220 nm light. Note that at zero bias, the responsivity varied little as the light intensity, as shown in Figure 3. A high response time was also observed.

### 2.2.3. Asymmetrical interdigital-finger SPD

By combining the merits of the MSM structure and the CSPD, two-mode photodetector SPD with interdigitalized-finger (IDF) Ohmic and Schottky contacts were created [73], as shown in Figure 4(a). The IDF-SPD can be operated at either reverse or forward mode. The IDF-SPD has a high photoresponsivity as a photoconductor at forward biases due to the Ohmic contact nature and high speed at reverse bias due to the Schottky contact nature. Like a CSPD, the dark current of the IDF-SPD could be as lower as <10^-13 A at reverse biases; while due to the ultra-wide bandgap energy of diamond, a low dark current as low as 10^-12 A at forward biases.
up to ±30 V was also achieved. The low dark current was also due to the low boron content in the SCD epilayer and the sub surface pn-junction effect. Figure 4(b) shows the I-V characteristics of the IDF-SPD upon the 220 nm light illumination, showing a rectification ratio more than $10^4$ at ±5 V. The dependence of the responsivity on the reverse bias was similar to the symmetrical MSM detector, but different from the CSPD. The external quantum efficiency reached 20% at a reverse bias of 30 V and was larger than 100% for at the forward biases [58]. The response time measured by chopping at 100 Hz under 220 nm illumination light at a forward bias of −32 V was larger than 10 ms but small than 10 ms at a reverse bias of 32 V, as shown in Figure 4(c).

2.2.4. Photodiode based on p(i)n junction
Photodiodes based on p(i)n-junction is the most desirable structure for photovoltaic operation due to the fast speed and high responsivity. Koizumi et al obtained the first n-type diamond epilayer grown on the [111]-oriented diamond substrate by phosphorus doping and demonstrated the DUV LED diode [26,74]. The p-i-n photodiode was used to DUV or extreme UV detection. The DUV sensitivity at 200 nm was around 27.2 mA/W [75], much higher than that of the diamond SPD at zero bias. The photocurrent ratio between 210 nm and 310 nm was more than $10^4$ of the p-i-n photodiode at zero bias.
2.3. Spectra tuning

The multicolor optical sensing can find applications varying from imaging, surveillance, optical communication, remote control, to target identification. To achieve broad spectral response, simply doping diamond by boron or nitrogen is possible, however, the controllability to satisfy the $5S$ requirement is a problem. One good example is the 270 nm response induced by nitrogen. By simply assembling other semiconductors on an intrinsic diamond layer, the multi-color sensing can also be achieved with arbitrary spectral selection, as shown in Figure 5(a) [76]. By placing a $\beta$-Ga$_2$O$_3$ nanobelt on diamond, dual-wavelength solar blind photodetectors with cut-off wavelength at around 280 nm and 230 nm were demonstrated. Dual-band and three-band photodetectors for visible light and DUV light detection were also developed by integrating CdS nanowires or CdS nanowires and ZnO nanowires on diamond intrinsic layers, as shown in Figure 5(b,c). The detectivity was as high as $10^{14} - 10^{15}$ Hz$^{1/2}$/W in the UV region. The above method circumvents the problem of the generation of interface states between diamond and the other semiconductors.

By depositing $\beta$-Ga$_2$O$_3$ on diamond, self-powered solar-blind photodetectors based on diamond/$\beta$-Ga$_2$O$_3$ heterojunctions was reported. Under zero bias, the photodetectors showed a peak responsivity of 0.2 mA/W at 244 nm and a sharp cutoff wavelength of 270 nm [77]. Other oxides/diamond heterojunctions were also reported to broaden the spectral response of diamond, such as by depositing TiO$_2$ or NiO thin films on diamond [78, 79]. Nevertheless, the interface of the heterojunctions should be investigated.

2.4. Other factors affecting the photoresponse properties

In addition to the device design, the photoresponse properties of diamond DUV detectors can also be tailored by the impurities and their concentration in diamond, the surface states, materials design, metal contacts, and post annealing often adopted. The external applied bias also affects the photoresponse properties of diamond DUV detector, as discussed in the next section.

The diamond type or impurities in diamond affects the photoresponse properties. Most of the commercially available SCD diamond substrates at this stage usually show poor photoresponse properties. The high-pressure high temperature (HPHT) type-Ib diamond with oxygen-terminated surface shows photoresponse dominated by nitrogen and the quantum efficiency at DUV region is as low as ~ 0.1%. The nitrogen content in natural type IIa diamonds is still too high to have a good spectral selectivity. Therefore, homoepitaxially grown diamond layers are necessary to have DUV detector meeting the demand of $5S$ requirements. When the common type-Ib diamond is used as the substrate, the spectral response of diamond DUV detector depends on the epilayer thickness. For the submicron thin diamond epilayer, the shoulder at around 270 nm along with the visible light response at 450–600 nm from the type-Ib diamond substrate is observed. The 270 nm photoresponse disappears for the intrinsic diamond epilayer with a thickness larger than 5 µm.

Another important factor influencing the photoresponse properties is the surface termination. Mostly, the surface of diamond is oxygen (O)-terminated or hydrogen (H)-terminated diamond for diamond DUV detection. Oxygen-termination is desirable to achieve low dark current. Hydrogen-termination always leads to a
high dark current due to the existence of 2-dimensional hole gas (2DHG) on the diamond surface. The photocurrent could not be distinguished from the dark current for the photodetector fabricated on intrinsic H-terminated diamond layer [80]. By using H-plasma treating the type-Ib diamond substrate, one can tailor the overall photoresponse such as the dark current, sensitivity, and spectral response [6]. The H-plasma markedly enhanced the DUV photocurrent by $10^5$ [81–83]. The highest responsivity reached 230 A/W [81] and the 210 nm/visible light injection ratio reached $10^4$.

2.5. Photoconductive gain mechanism

Without considering avalanche effect, photoconductivity gain requires circled carriers in the electric circuit or carriers injection from the contact to the semiconductor. For example, a photoconductor with Ohmic contacts can show gain. Ideally, no photocurrent gain occurs for a photodiode at reverse biases if the avalanche effect does not appear [84,85]. The photocurrent gain occurs in the case of deep defects either in the semiconductor bulk or on the semiconductor surface. However, PPC is often accompanied [86].

We observed photoconductive gain for both SPD and MSM photodiode at reverse biases, even the diamond surface was O-terminated [87]. This was due to the lowering of the interface barrier height or narrowing of the depletion width by the interface states. For a MSM photodiode, the photoconductive gain depends on the incident DUV light intensity or the applied bias magnitude. It was found for a MSM photodiode fabricated on O-terminated diamond surface that (i) no gain appeared at low bias (i.e. 5 V), (ii) gain came out at high biases (i.e. 32 V) with the appearance of PPC, and (iii) the gain reduced with temperature increasing. The gain in a diamond MSM photodiode was attributed to the charge trapping at the metal/diamond interface during DUV illumination. These charges shrunk the depletion region between the metal and diamond. Therefore, carriers tunneled through the interface through thermionic-field emission (TFE) or field emission (FE) at high biases.

A huge gain $>10^4$ was also observed on highly boron doped ($>10^{17}$ cm$^{-3}$) diamond epilayer grown on a type-Ib diamond substrate [86]. By analyzing the temperature-dependent photocurrent, an electron trap with a thermal energy of 1.37 eV was extracted for the gain and PPC. On the other hand, the PPC could be quenched by visible light illumination with a threshold energy at around 2 eV. Due to sub-surface pn-junction between the epilayer and the nitrogen-containing diamond substrate, the device could be electrically polarized, which led to the appearance of absolute transient negative photocurrent (TNPC) at zero or weak electric fields, even the incident light is in the DUV region.

2.6. Comparison of diamond DUV detectors and applications

In order to make the review an integrity, we compare the photoresponse properties of the photodetectors based on both SCDs and polycrystalline diamonds [57,88] in Table 1, although not all the diamond detectors are shown. A more complete comparison can be found literature [90]. To summarize the points

1. Generally, SCDs is no doubt the most ideal candidate for DUV detectors to satisfy the 5S requirement in all forms of diamonds.
2. The photoresponse properties still vary from lab to lab due to the quality of the diamond crystal and device processing.
3. The overall performance of SCD DUV detectors can be readily tailored through surface modification or bulk doping, device structures and external applied bias [87,91]. Pure diamond with H-terminated surface usually shows large dark current, difficult for DUV detectors. However, a pure diamond layer with H-termination grown on a type-Ib SCD substrate forming the subsurface junction can exhibit low dark current, high DUV photocurrent, high DUV/visible rejection ratio, and fast response time.
4. In the MSM photodiodes, the applied bias could also tailor the responsivity through interface states or avalanche breakdown. The metal-diamond interface should be optimized.
5. Although polycrystalline or nanocrystalline diamonds have intrinsic drawbacks of the existence of sp$^2$ carbon, some exciting results were reported on UV detectors based on these diamonds by proper surface modification or nanostructuring [89]. For example, boron-doped ultrananocrystalline diamond nanowires functionalized with the platinum nanoparticles formed self-powered UV photodetectors with an ultrahigh photoresponsivity of 388 A/W at 300 nm wavelength, a fast response time around 20 ms and a good UV/visible rejection ratio of about 5 orders of magnitude under zero-bias condition were demonstrated [89].
6. Certain applications of SCD DUV detector are feasible, although there is still much room to improve the photoresponse properties of SCD photodetectors through devices designing, crystal quality control, and surface modification of the SCD layers.

Finally, we list some examples of applications of diamond DUV detectors. One simple application is for high-power DUV lamp or laser monitor with high stability. Diamond DUV detectors for flame sensing by using nitrogen impurity in diamond was also demonstrated [88]. Although the cut-off wavelength of diamond is at
36

M. LIÃO

225 nm, not suitable for flame sensing, the practical cut-off wavelength was tailored to be 270 nm by depositing a boron-doped diamond epilayer on type Ib-diamond substrates. The diamond DUV detector was also adopted for UV imaging, as shown in Figure 6, which may disclose information that visible light cannot detect on the objects surface [77]. Another exciting application of diamond DUV detector is the solar-blind communication system that showed high anti-interference ability with a −3 dB cutoff frequency of 1970 Hz [83].

3. Diamond MEMS

Diamond has demonstrated itself an ideal material to for MEMS applications with unprecedented performance and high reliability due to its outstanding mechanical strength, thermal conductivity, electronic properties, and chemical inertness. Great efforts and progress have been made in the polycrystalline, nanocrystalline and ultra-nanocrystalline diamond to fabricate diversiform diamond MEMS configurations [92–97]. The applications of polycrystalline diamond includes pressure sensors, switch, and actuators. Single-crystal diamond can circumvent the effect of grain boundaries and other carbon phase in terms of the extreme device performance.

Here, we review the recent results on SCD MEMS/NEMS. These contents include the micromachining of SCD, the mechanical energy dissipation mechanisms, the improvement of the quality (Q) factors of the SCD resonators and the sensing applications.

3.1. Micromachining of single-crystal diamond MEMS/NEMS

Since diamond is chemically inert and has extremely high mechanical strength, it is difficult to apply the conventional micromachining process for Si and other wide bandgap semiconductors to SCD. Mainly, three approaches were developed for the fabrication of SCD mechanical resonators: smart-cut technique based on high-energy implantation [98], direct thinning SCD plates through bonding on an insulator substrate called diamond-on-insulator (DOI) method [99,100], and

| Material | Device | Dark current | Responsivity (A/W)@220nm | 220nm/visible ratio | Speed | Voltage (V) | Ref |
|----------|--------|--------------|--------------------------|---------------------|-------|-------------|-----|
| SCD      | MSM    | 0.1 pA       | 0.177                    | $10^0$              |       | 5           | [66]|
| SCD      | MSM    | <0.1 pA      | 6                        | $10^0$              | 0.3s  | 3           | [67]|
| B-SCD    | MSM    | 10 pA        | 230                      | $10^0$              | PPC   | 10          | [81]|
| SCD      | MSM    | 5 µA         | 21.8                     | ~$10^4$             |       | 50          | [82]|
| B-SCD    | SPD    | <0.1 pA      | 0.99                     | $10^0$              | PPC   | 3           | [29]|
| SCD      | pin diode | <0.1 pA     | 0.027                    | $10^0$              |       | 0           | [75]|
| UNCD     | Schottky + Pt | 0.07 µA   | 388 at 300 nm           | $10^0$ (300 nm/vis) | 20ms  | 0           | [89]|
| PCD      | MSM    | <0.1 nA      | 0.1                      | $10^0$              | 150ns | 0.1–10      | [57]|
| PCD      | MSM    | 1 pA         | 0.1                      | $10^0$              |       | 10–50       | [59]|

Table 1. Comparison of photoresponse properties of recently reported diamond-based UV detectors.

Figure 6. Diamond/β-Ga$_2$O$_3$ heterojunction photodetector for UV imaging at 0 V (a) Schematic illustration. (b) The image of the object with letters “UV” on a black paper. (c) Image obtained from the imaging system [77]. © 2018, Royal Society of Chemistry.
angled etching [101,102]. In the DOI method, the Q factors of the SCD cantilevers could reach over one million [99,100]. The DOI method was started from a smooth (RMS < 0.5 nm) and thin (20 µm) commercial SCD plate. In the fabrication, a thin SiO₂ layer (30 nm) was deposited on one side of the diamond plate [99]. Or one could use hydrogen silsesquioxane (HSQ) resist as an intermediary for diamond and SiO₂/Si bonding [100]. The diamond layer was then thinned to the designed thickness, which can be 0.1 µm–2 µm by using a reactive ion etch/inductively coupled plasma (RIE/ICP) etch. Next, the thin SCD was patterned to form the cantilever structure by photolithography. A second metal (gold or aluminum) mask was deposited on the patterned DOI substrate as a mask for RIE etching. Finally, the SCD cantilevers were released by in a buffered hydrofluoric acid to selectively remove the SiO₂ layer. Alternatively, the SCD plate can be clamped by two quartzs to form the sandwich structure. Then, the SCD was thinned to be the designed thickness, i.e. <500 nm by RIE. Finally, the quartz can be etched to form the SCD cantilever.

Figure 7 shows the cross section of the multilayer DOI structure on Si and the obtained SCD cantilevers. One advantage of the DOI method is the ability to maintain the high crystal quality of the initial diamond plate.

Freestanding SCD nanoscale mechanical resonators was also achieved by using angled etching technique in a plasma [101]. In this approach, the SCD was firstly patterned to form the designed geometries masked with metals, then, the masked SCD plate was etching by plasma, and finally, a second anisotropic etch step was performed at an oblique angle through a Faraday cage with θ ~ 45° to release the nanostructures [103]. The fabrication method and the SCD resonators were illustrated in Figure 8.

In our group, the fabrication of SCD mechanical resonators was performed by borrowing the idea for freestanding SCD plates and optical guide [104–107]. We utilized high-energy ion implantation to generate graphite-like carbon buried in the diamond substrate. By removing the buried graphite-like carbon layer, the SCD MEMS resonators were achieved. This approach was called smart-cut method. An outstanding feature of the smart-cut method is the all SCD MEMS/NEMS nature, the controlled dimensions from nanoscale to microscale, and high reproducibility [108]. We started the fabrication from a high-pressure high-temperature (HPHT) type-Ib SCD substrate with high-energy implantation. A homoepitaxial diamond layer was then grown on the ion-implanted SCD substrate. During the growth, the buried damage layer was transformed into graphite-like carbon. One can annealed the sample in an ultra-high vacuum chamber (~10⁻⁷ Pa) to reduce the ion impinged defects within the diamond. The sample was then patterned by metallic layers such as aluminum or tungsten carbide or gold as the mask for dry etching in an oxygen plasma. Finally, the SCD mechanical resonators were released in boiling sulfuric acid or by electrochemical (EC) etching. This process led to the SCD mechanical resonators on SCD substrate (SCD-on-SCD). Figure 9(a) displays the batch fabrication process for the SCD MEMS resonators.
Figure 9(b–d) show the scanning electron microscopy (SEM) images of the SCD bridges and cantilevers with different dimensions in microscale or nanoscale. The diamond bridges and cantilevers are constituted of two layers: the homoepitaxial diamond layer and the substrate type-Ib diamond layer separated from the original substrate.

3.2. Crystal quality of single-crystal diamond mechanical resonators

The disappearance of the feature peak of 1332 cm$^{-1}$ in the Raman spectrum of the diamond after ion implantation disclosed the ion-implantation induced disorder and graphitization [98]. After releasing the cantilevers, only the feature peak at 1332 cm$^{-1}$ of diamond was observed. The SCD nature was confirmed by high-resolution transmission electron microscopy (HRTEM) images, which also identified the diamond-graphite-like carbon-diamond structure [98,108]. We note that the point defects within the type-Ib SCD substrate originated from ion irradiation cannot be excluded out. In addition, the graphite-like structure was confirmed by selected area electron diffraction. Cathodoluminescence (CL) measurements conducted from different locations of the SCD plate with SCD resonators at room temperature further revealed the high-crystal quality of the cantilevers [98,108].

3.3. Mechanical resonance of SCD MEMS

The spectrum of mechanical resonance frequency offers the information of Young’s modulus and Q factor of the resonators. Both are fundamentally key factors for
MEMS/NEMS resonators, which determine the sensitivity and noise level of MEMS/NEMS that underlies timing references, frequency sources, atomic force microscopes, gyroscopes, and mass sensors [109–111].

The actuation method of the mechanical resonators can be piezoelectric [112], capacitive [113], magnetomotive [114], photothermal [115] and electrothermal [116], among which the piezoelectric method is mostly adopted due to the simplicity. One can use either optical or electrical method to measure the resonance properties of the SCD mechanical resonators. The Laser Doppler Velocimetry (LDV) is the mostly employed optical technique to measure the mechanical resonator frequency, which is based on the measurement of the instantaneous velocity the target object.

3.3.1. **Resonance frequency of the SCD mechanical resonators**

The resonance frequency of the SCD cantilevers fabricated by the smart-cut method [98,108,117] were described here. Both high-energy carbon ions (180 keV) and hellion ions (1 MeV) were adopted for the SCD cantilevers fabrication. SCD cantilevers with different widths from 3.1 to 10 µm, length from around 30 to 206 µm, and thickness from 0.68 to 1.7 µm, were analyzed.

The resonance measurements of the SCD cantilevers were performed in a high vacuum (~10⁻⁵ Torr) to avoid the air/gas damping. The diamond cantilevers were actuated by applying a radio-frequency signal to the piezoceramic element. The optical images of the SCD cantilever and a typical fundamental resonance frequency spectrum of the SCD cantilever is shown in Figure 10(a,b). The SCD cantilever was a typical harmonic oscillator, which can be fitted by a square-root of Lorentzian profile with a centred resonant frequency. The resonance frequency of the SCD cantilevers is consistent with the Euler-Bernoulli theory with a law of 1/L² [117–119], as shown in Figure 10(c)

\[
f = \frac{k}{L} \sqrt{\frac{E}{\rho}}
\]

where \(k = 0.162\) when the resonator is a cantilever in the first vibration mode, \(E\) is the Young’s modulus, \(\rho\) is the mass density, \(t\) is the thickness and \(L\) is the length of the cantilever. The slight deviation between the experimental and theoretical frequency might be the existence of stress in the cantilevers. The consistence of the experiments with the theoretical fitting reveals the high reproducibility of the smart-cut method for the fabrication of SCD mechanical resonators. The Young’s modulus of the SCD-cantilevers extracted by the length-dependent resonance frequency was around ~1100 GPa, close to that of bulk SCD (1143 GPa).

3.3.2. **Mechanisms of energy dissipations in SCD MEMS resonators**

The mechanical energy dissipation determines the Q factor, a key figure-of-merit of a mechanical resonator, which ultimately governs the device sensitivity such as force, mass, and displacement etc. For example, the minimum detectable force for a normal rectangular cantilever can be expressed as [119]

\[
F_{\text{min}} = \left(\frac{wL^2}{LQ}\right)^{1/2} (k_BTBE_B)^{1/2} (E\rho)^{1/4}
\]

where \(E\) is the Young’s modulus, \(\rho\) is the mass density of the resonator, \(B\) is the bandwidth, and \(w\) is the width of the cantilever.

Usually, one can obtain the Q factor by fitting resonance frequency spectrum with a Lorentzians shape to extract the full-width at half-maximum (FWHM), as defined by

\[
\Delta f = \frac{f_r}{2} \Delta f
\]

where \(f_r\) is the resonance frequency and \(\Delta f\) is FWHM of the resonance spectrum. In order to clarify the energy dissipation mechanism, we usually consider the main dissipations by excluding others. The overall Q factor is a sum of all the dissipations like

Figure 10. (a) Optical image of the SCD cantilevers, (b) typical resonance frequency spectrum of a SCD cantilever. (c) Dependence of the resonance frequency on the cantilevers length with different thickness.
where $Q_{\text{air}}$, $Q_{\text{clamp}}$, $Q_{\text{TED}}$, $Q_{\text{bulk}}$, and $Q_{\text{surf}}$ are the Q-factors, which represent the loss mechanisms of air damping, clamping loss, thermoelastic damping (TED)[120], bulk, and surface losses, respectively. It was observed that for the SCD cantilevers fabricated by 180 keV carbon ion implantation, the Q factors were in the range of 3,000 to 7,000 and decreased with the cantilever length from 80 to 30 µm [117]. For the SCD cantilever with length longer than 80 µm, the Q factors tended to decrease. For SCD cantilevers fabricated by 1 MeV He ion implantation, it was observed that the Q factors were slightly lower than those of SCD cantilevers fabricated by carbon ion implantation. However, a similar behavior in Q-factor as the cantilever length was observed. The plot of Q factors vs $L/(wt^2)$ disclosed that the clamping loss was responsible for the short cantilevers [121]. A key point is that the Q factor of the SCD cantilever fabricated by the smart-cut method is limited by the bulk defects or surface effect dissipation induced by ion implantation [122,123].

### 3.3.3. Improving the Q factors

As revealed by the fabrication process, the smart-cut SCD mechanical resonators contain the homoepitaxial layer and the damaged substrate diamond layer by ion implantation. Two strategies can be used to improve the Q-factor of the SCD mechanical resonators: overgrowth of a high-quality diamond epilayer on the ion-implanted diamond substrate and the removal of the damaged layer at the bottom of the SCD cantilever. The dependence of the Q-factor on the epilayer thickness can be modeled by a two-layer structure. By growing a 1.81 µm-thick homoepitaxial layer, we achieved a Q-factor to 39,447 [124].

Expectedly, the total removal of the damaged layer would markedly improve the Q-factors of the SCD cantilevers. We developed an atomic scale etching method by annealing the as-fabricated SCD cantilevers at 500 °C in an oxygen ambient [125]. The etching effect can be monitored by the shift of the resonance frequency, as shown in Figure 11(a,b). From the shift of the resonance frequency, the etching rate of SCD was estimated to be around 0.25 nm/h at 500 °C for one side of the cantilever, corresponding to a carbon mass loss of $10^{-12}$ g/h. The Q-factor increased with the etching prolonged, as shown in Figure 11(c). After nearly 380 h etching, the Q factor was markedly improved from 10,000 to over 1,600,000. By using ring-down measurement, the Q factor reached over 430,000 for a 1.44 µm-thick and 100 µm-length SCD cantilever (Figure 11(d)). After further etching or cleaning by hydrogen plasma, the Q factor finally reached over one million [126], higher than those values reported for polycrystalline or nanocrystalline diamonds. The Q factor is comparable to that of by DOI method [100].
3.4. Diamond MEMS magnetic sensor

While the magnetic sensors based on nitrogen-vacancy by using the spinning effect are widely investigated [127], diamond MEMS magnetic sensor provides a different scheme using mechanical effect. The principles of MEMS magnetic sensors can be Lorentz force [128] or torque force [129] or effective Young’s modulus change (delta-E effect) of the MEMS resonator under applied magnetic fields [130]. The merits of MEMS-based magnetic field sensors are the small dimensions, batch fabrication, flexibility in device design, and integration with electronics. Diamond MEMS magnetic sensor integrated with a magnetostrictive material having high Curie temperature can overcome the weakness of Si MEMS with low reliability at elevated temperatures.

The only SCD MEMS magnetic sensor was realized by integrating a giant magnetostrictive galfenol (FeGa) thin film on a SCD mechanical resonator based on the delta-E effect. Upon external magnetic fields, the resonance frequency of the FeGa/diamond mechanical resonator experienced a shift due to the stress applied on the resonator, as shown in Figure 12(a). The magnetic sensitivity depends on the resonance frequency and the Q factor of the mechanical resonator. The FeGa film (80 nm thick) deposited on the SCD substrate had excellent magnetic properties with a coercive field $H_c$ as low as 26 Oe and a saturation magnetization $M_s$ of 183.8 emu/g [131]. The magnetic sensitivity is extracted from the shift of the resonance frequency of the resonator as the applied magnetic field, as displayed in Figure 12(b,c). A magnetic field sensitivity of 4.83 Hz/mT and a detectable force of $2.14 \times 10^{-12}$ N were achieved at room temperature for the FeGa/diamond cantilever. Due to the large lattice mismatch between FeGa and diamond, the FeGa/SCD MEMS composite resonator could only be operated up to 300 °C [132].

By adding a buffered Ti layer between the FeGa thin film and diamond, both the thermal stability and magnetic sensitivity of the diamond MEMS magnetic sensor were improved [133]. The FeGa/Ti/diamond multilayer-structured magnetic sensor presented a sensitivity 35.2 Hz/mT and a noise level of 9 nT/Hz at room temperature. The sensitivity increased to 71.1 Hz/mT and the noise level had little degradation with a value of 10 nT/√Hz even at 500 °C, as presented in Figure 13. The magnetic sensitivity can be further improved by doping FeGa with boron to be as high as 152.1 Hz/mT [134]. Future work should be performed by optimizing the resonator dimensions, thickness of the magnetic thin film, interface control between diamond and magnetic thin film, and reduction of the defects in diamond. The operation temperature of the diamond MEMS magnetic sensor is comparable to those of Hall sensor based on III-nitride, but with better thermal stability. The sensitivity of the delta-E effect magnetic sensor is also higher than those of based on Lorenz force. The merits of the diamond MEMS magnetic sensor over other type magnetic sensors were compared in Table 2 [133].

4. Summary and outlook

In this paper, DUV photodetector and high-reliability magnetic sensors base on SCD are reviewed. These two fields, along with the radiation detector, are the closest electrical devices to practical applications for diamond semiconductor at this stage. The SCD-UV detector can satisfy the SS requirement by high quality diamond crystal, impurities engineering, interface controlling, and proper device design. When thick high crystal quality is not available, one can tailor the epilayer structure and metal/diamond interface to tailor the photoresponse properties of the diamond DUV detectors. The sensitivity of the diamond DUV sensitivity can be further improved by using 3-dimensional electrode structures [135]. To extend the applications of diamond detectors into more fields, the combination of diamond film with

![Figure 12](image-url)
other semiconductors provides a promising route to broaden the spectral response.

Single-crystal diamond for MEMS/NEMS application is achieved by using a smart-cut method with well-controlled device dimensions. The smart-cut method provides the diamond-on-diamond device concept for MEMS/NEMS able to operate under harsh environments, which use a monolithic and highly reproducible fabrication process. For the as-fabricated SCD mechanical resonators, bulk defects and surface effect ultimately determined the Q factor. By removing the defective layer, the Q-factor increased from ~10,000 to over one million. The intrinsic Q-factor is much better than any existing semiconductor at room temperature. The SCD MEMS resonators were successfully applied to high-reliability magnetic sensor, which can be operated at 500 °C with high reliability. In the future, on-chip SCD MEMS/NEMS sensor would be developed. More applications of SCD MEMS in chemical, medical or biologic fields, and quantum information is expected to be explored.

Diamond has shown as an outstanding electronic and mechanical material for decades. Since the invention of CVD growth technique for thin film growth, great efforts have been made in the growth of SCD wafers on foreign substrates. Nevertheless, until recently, encouraging progress has been achieved on iridium thin film with a size of 4 inch [13], although the defects are still needed to be reduced. The size of homoepitaxial diamond layer is also expanding, especially based on the mosaic method. The large size SCD wafer in the future could facilitate the development of diamond MEMS sensors, in which the point defects are not so fatal as electronic devices.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

**Notes on contributor**

Dr. Meiyong Liao is now a principal researcher in National Institute for Materials Science (NIMS), Japan. He received the doctor degree of Materials Science in Institute for Semiconductors, Chinese Academy of Science (Beijing, China) in 2002. After 2-year visiting researcher in Kyoto University, Japan, he joined diamond research group at NIMS in 2004. In

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**Table 2. Comparison of high-temperature magnetic sensors. The references inside this table can be found in Ref. [133].**

| Magnetic sensor | Materials       | Magnetic sensitivity | Noise level            | Working temperature | Thermal reliability |
|-----------------|-----------------|----------------------|------------------------|---------------------|---------------------|
| AMR             | FeNi/Si         | –                    | -2.6 nT/√Hz            | 498 K               | Fair                |
| Hall            | Si              | –                    | >820 nT/√Hz            | 673 K               | –                   |
| Hall            | AlGaN/GaN       | –                    | 35 μT/√Hz              | 873 K               | Poor                |
| Hall            | AlGaN/GaN       | 67 V/(A·T)           | –                      | 673 K               | Fair                |
| Hall            | AlGaN/GaN       | 80 V/(A·T)           | –                      | 523 K               | Poor                |
| Hall            | 4H-SiC          | 80 V/(A·T)           | –                      | 770 K               | Good                |
| Fluxgate        | Cu coil         | –                    | 0.79 nT/√Hz            | 523 K               | Good                |
| MEMS            | FeGa/Ti/SCD     | 71.1 Hz/mT           | 10 nT/√Hz              | 773 K               | Very good           |

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**Figure 13.** (a) Resonance frequency shift with the external magnetic field at different temperatures of the FeGa/Ti/SCD cantilever, (b) dependence of resonance frequency shift on the temperature, (c) and (d) noise level at room temperature and 500 °C, respectively [133]. © 2020, American Chemical Society.
2008, he was employed as a permanent researcher in NIMS. He had also been a visiting researcher (2008) at CNRS, France and Marie Curie Research Fellow (2014–2015) in Aston University, England. His research interest includes wide bandgap semiconductor materials (mainly diamond), photonic and electronic devices, MEMS/NEMS, and device physics.

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