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Single crystal diamond photodiode for soft X-ray radiometry

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ABSTRACT

Method is presented to obtain current-mode responsivity from diamond photodiode in the soft X-ray range (0.25–7 keV). Pulsed bias and blocking contacts are used to mitigate artifacts of charge trapping and photoconductive gain. Mean electron-hole pair creation energy is measured from experimental data to be 13.25 ± 0.5 eV. Responsivity of diodes made from commercially available 500 μm thick single-crystal diamond (under conditions described) is reported.

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1. Introduction

Diamond has been explored as a possible sensor material for X-rays for several decades. Features which make it particularly attractive for use as a soft X-ray sensor material include its high thermal conductivity and melting point (making it robust in high heat load environments), its large band gap of 5.5 eV (making it insensitive to visible light), its relatively fast response [1], and its hardiness against radiation damage [2,3].

Motivation for development of diamond electronics has been strong in a number of fields, with the RD42 effort of the Large Hadron Collider being one of the principle recent thrusts [2,4–6]. Additional applications-based motivations come from high energy density physics [7–13], accelerator diagnostics and design [14–16], and astrophysics and solar astronomy [17]. In response to these demands, fabrication of high-purity, single crystal diamond is now possible using chemical vapor deposition, yielding a charge collection distance approaching the available sample size [18].

Despite these efforts, even the highest quality diamond materials are capable of trapping charge, thus losing collection efficiency of derived detectors. Such charge trapping leads to recombination loss and nonlinear (photoconductive) gain [19,20]. This problem may be more severe than for other semiconductors since its relatively large bandgap can permit deep traps which cannot detrap thermally. In natural diamond, nitrogen impurity leads to hole traps [21]. While ultra-low nitrogen content synthetic diamond is commercially available, other impurities or defects may also still lead to charge trapping. In addition, the formation of metal contacts raises further questions regarding type, chemistry, processing and geometry, which are still not fully understood. In comparison to silicon, diamond is a newer and therefore less understood electronic material, and thus is more challenging when it comes to detector construction and operation.

The aim of this paper is to report successful mitigation of charge trapping by applying pulsed bias during pseudo-continuous soft X-ray illumination, to provide a linear and calculable responsivity (photocurrent per incident light power) in the 0.25–7 keV photon energy range.

2. Experimental

Single-crystal "detector grade" diamond samples were obtained from DDL, a subsidiary of E6/DeBeers. This grade of diamond has a specified nitrogen impurity of less than 5 ppb. These have nominal lateral dimensions of $4\,\text{mm} \times 4\,\text{mm}$ and thickness of 500 μm. Thickness was verified by physical measurement. Surface normal orientation is stated by the vendor to be {1 0 0}, with edges either ⟨1 1 0⟩ or ⟨1 0 0⟩. Upon receipt, diamond sample surfaces were prepared by boiling in chromic acid, followed by ammonium hydroxide/acid/peroxide wash, to remove graphitic carbon and residual metal, and to yield an oxygen-terminated surface. Metallization was then performed on each of the two large sides by argon-ion sputtering to produce films ranging in thickness from 15 to 50 nm in a circular area with

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3 mm diameter near the center of each side. In this paper, only blocking (non-annealed) contact behavior is discussed. However, it should be mentioned that annealed (ohmic) contacts were also tested and found to yield photoconductive gain and its attendant sublinear responsivity for electron transmission through bulk diamond. These observations confirm the contact type as ohmic in the annealed case, and blocking in the un-annealed case. Metal films measured in this paper include Ti/Pt, Mo, Nb, and Cu.

Metallized samples were installed to a holder with copper annular electrodes, set in firm contact to each surface using conical spring washers. Secondary annular electrodes spaced 0.5 mm from each primary electrode were biased at −30 V for suppression of photoelectron emission. (Photoelectron response was also measured (under +30 V bias) and found to be highest at low energies, yet negligible compared to diamond diode response in all cases measured here). The sample and illumination geometry is indicated in Fig. 1.

Soft X-ray photons were provided by beamlines U3c and X8a at NSLS [22–24]. These beamlines are instrumented to provide highly monochromatic, pseudo-continuous photons over a wide range of soft X-ray energies, and measurement of beamline flux using calibrated silicon photodiodes operating in biasless (self-depleting) DC photocurrent mode, with an overall accuracy of 2–5% [25]. Current measurements are made possible using calibrated Keithley 617 electrometers. In order to maintain high monochromaticity, various filters and mirrors are automatically selected as the photon energy is scanned, resulting in several abrupt changes in flux and a total span of 1 nW–10 μW/mm^2 over the 0.25–7 keV photon energy range. The X-ray beam is collimated to 400 μm diameter for illumination of central portions of the 2 mm diameter exposed portion of the metallized diamond samples in the holder. All measurements are performed in the vacuum beamline endstation at an ambient pressure of 2 μTorr or less.

Carriers freed in the diamond material by exposure to soft X-rays incident at one electrode are accelerated towards the opposite contact by an applied field. If positive bias is applied to the incident electrode, positive transmitted hole current is measured at the downstream contact. Likewise, negative bias applied to the downstream contact permits measurement of (negative) transmitted hole current at the incident electrode. Reversing the polarity in either case switches the measurement to one of electrons.

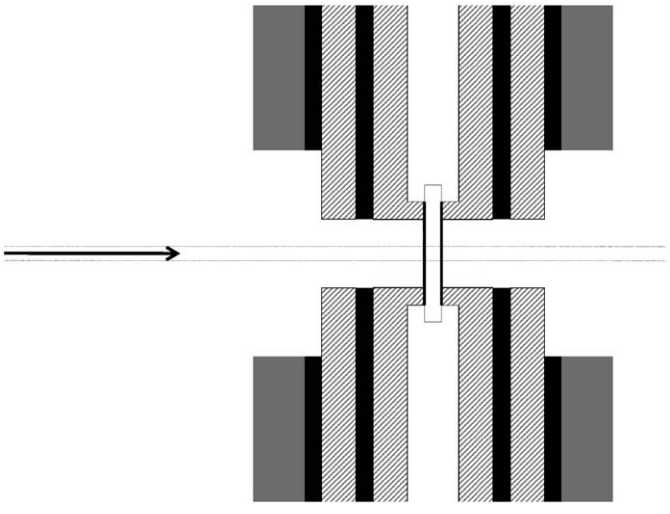

Fig. 1. Cross-section of the annular diamond sensor holder, showing the geometry of the diamond, electrodes, holder, and illumination. The 0.4 mm wide X-ray beam illuminates the diamond sample from the left. The diamond, at the center, is 0.5 mm thick and 4 mm wide, with central 3 mm diameter metallization on the incident and transmission sides. The four hatched regions indicate addressable copper electrodes: two contact the metallized surfaces of the diamond, and two more are used to suppress photoemission. The thick black areas indicate ceramic insulator material, and the gray areas indicate the grounded outer holder.

Initially, constant DC bias was used. However, it was quickly observed that under continuous soft X-ray illumination, application of bias (from initially zero field) yielded an instantaneous photocurrent which decayed within 1–2 s to a steady-state value which was lower by roughly a factor of 5 or more. This observation was found for both electron and hole transmission with blocking contacts (Ohmic contacts were found to yield a higher steady-state value for electrons via photoconductive gain). Reduction of the field during exposure to the ionizing radiation was found to consistently restore the diamond to a state in which returning the bias yielded again a high instantaneous photocurrent. In an effort to capture this instantaneous value as a continuous value, bias was applied to the sample in the form of a square wave with a characteristic "on" voltage (the "off" voltage being zero), frequency, and duty cycle, as indicated in Fig. 2. This bias was accomplished using a standard signal generator (capable of providing no more than 8 V), combined with a linear amplifier (from FLC electronics) providing fixed gain of 20× or 100×. A 10 nF capacitor to ground was installed in parallel to the signal chain in order to filter out the high frequency spikes injected at the switch points by this biasing scheme, and therefore to help the electrometers provide accurate DC photocurrent measurements. Observed responsivity is reported as the observed value (photocurrent per light power), normalized by the applied duty cycle.

Our explanation of this behavior is as follows. Under constant bias, charge trapping leads to a flux and time dependent reduction of the electric field in the diamond. When the electric field is low enough that the diffusion of carriers is comparable to their drift, carriers will recombine (at the incident electrode) and be lost, reducing the effective responsivity. For pulsed bias, carriers created by the X-ray beam during the "off" time move under the influence of the field generated by the trapped charge, ultimately recombining with and neutralizing the trapped carriers, leaving the diamond field-free when the bias switches back on. It should be noted that for electron transmission, the optimal cleaning time is observed to be much longer than for hole transmission, and that the responsivity is consistently lower as well under otherwise identical conditions. These observations suggest that electrons have a larger probability of being trapped and that holes are therefore the majority carrier in these devices.

A number of tests were performed, spanning a wide range of values for frequency, bias ("on" level), and duty cycle, ultimately yielding a set of parameters under which responsivity could be reliably measured for the diamond diodes.

3. Results

Example results are shown in Figs. 3 and 4. Below 4 keV photon energy, we found that hole responsivity could be reasonably determined using up to 98–99% duty cycle with 100 Hz frequency (0.1–0.2 ms "off" time for cleaning). However, at higher energies (5–7 keV), where photon absorption occurs deeper into the bulk of the sample and flux at the beamline begins to drop off, a lower duty cycle (50% or less) appears to be required in order to ensure complete charge cleaning during the "off" period (up to 5 ms). Above ~100 V bias (field of ~0.2 MV/m), the hole responsivity does not increase more significantly with increasing voltage. For holes, frequency dependence was found to be relatively weak, so that frequencies in the range 1 Hz–100 kHz could be used (the 100 kHz limit comes from the bandwidth of the amplifier

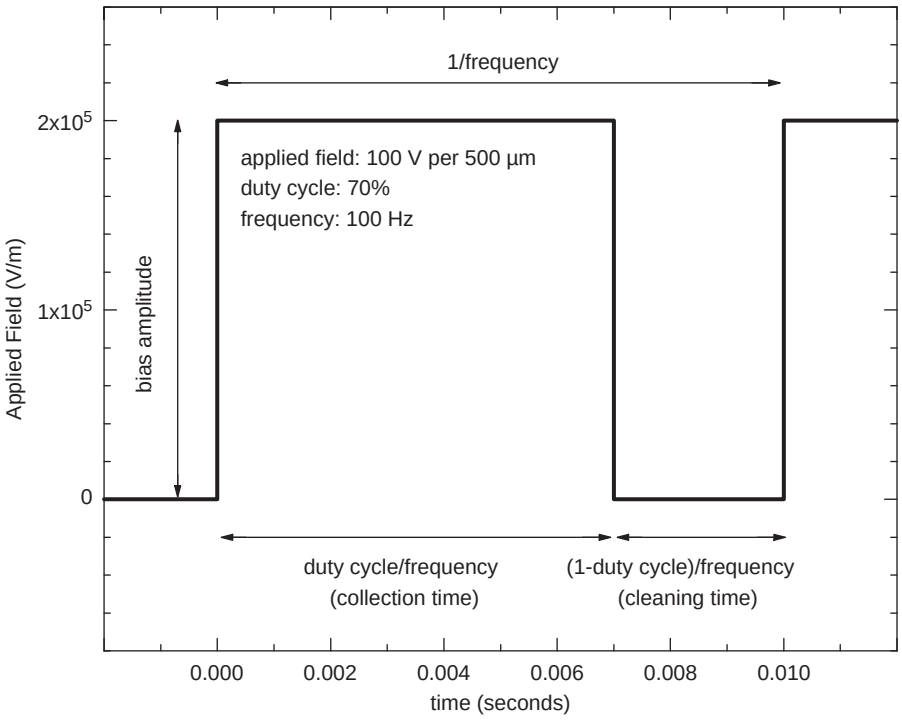

Fig. 2. Illustration of the biasing waveform, applied for sequential collection of photo-induced charge and charge detrapping. This bias trace shows characteristic parameters of frequency (period), "on" and "off" levels, and duty cycle ("on" and "off" times).

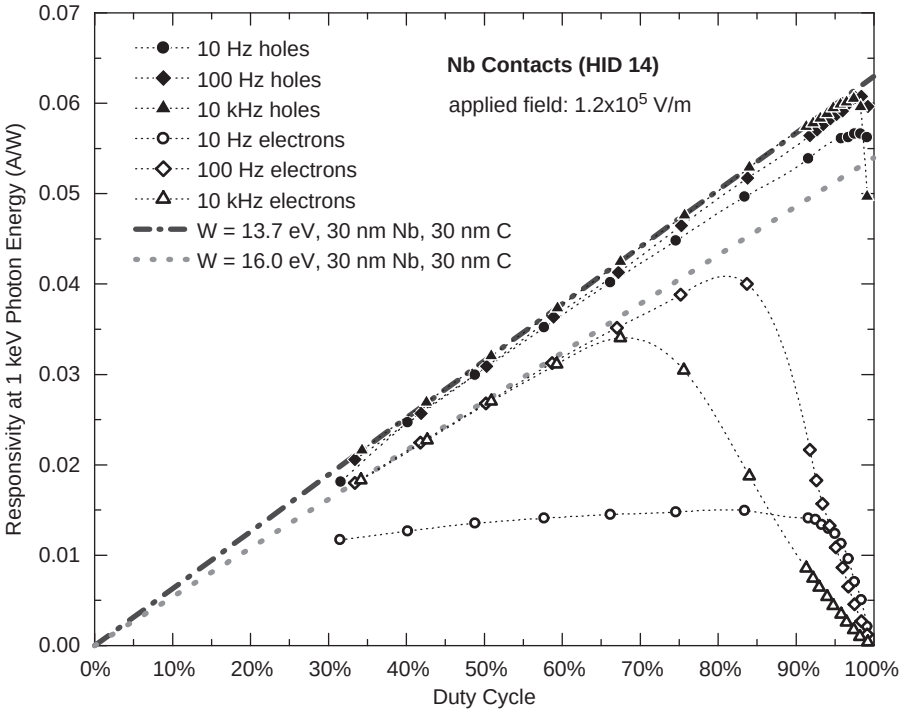

Fig. 3. Responsivity versus frequency and duty cycle for holes and electrons, for the example of non-annealed niobium contacts.

used—the 1 Hz limit comes from the electrometers); 100 Hz was a typical value used the measurements.

For electrons, complete charge collection through the sample could not be achieved with any combination of bias and duty cycle. Responsivity was found to be linear with duty cycle only for lower values than for holes (these samples appeared linear below roughly 50%). The frequency appears to be optimal at ~100 Hz for the flux levels used, corresponding to 5 ms for each of collection and cleaning at 50% duty cycle. At the same applied field and 50% duty cycle, electron responsivity consistently underperforms holes by 5–20% due to increased trapping. This behavior is consistent with the observation of photoconductive gain for diamonds with ohmic contacts under electron biasing conditions, which will be discussed in a subsequent work.

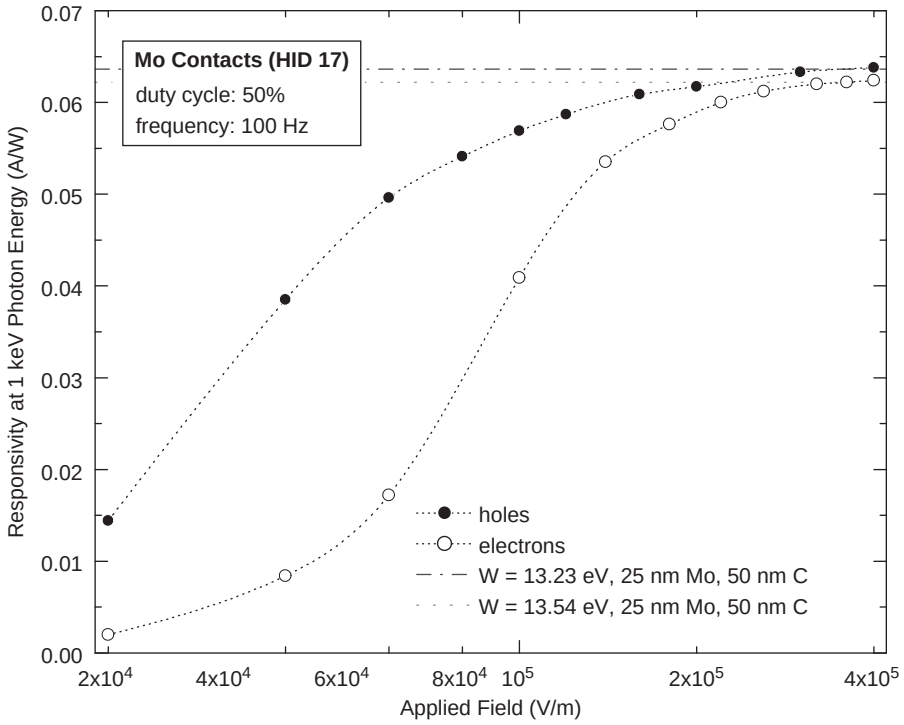

Fig. 4. Responsivity versus applied "on" bias for holes and electrons, for the example of non-annealed molybdenum contacts. In this case the duty cycle was 50% and the frequency was 100 Hz.

The responsivity behavior of the diamond samples was found to be largely insensitive to the composition of the metal contacts, as long as the contacts remained blocking (not annealed). Differences between diamond samples with blocking contacts appear in the characteristic photoelectric absorption behavior of the window (contact and dead layer) materials.

Responsivity for these samples can be modeled using a simple function which includes the characteristic material thicknesses and the mean electron-hole pair creation energy W. Fits to the experimentally measured responsivity data allow determination of these parameters. Using the holes responsivity data for several diodes, we have found W values in the range of 13.2–13.3 eV with an uncertainty of roughly 4%, in agreement with several previous estimates [26–28].

We have also found a significant carbon edge drop in the responsivity versus photon energy data. This behavior is attributed to charge recombination near the window electrode. Since the diffusion velocity slows as the cloud of carriers becomes larger, at a given field, more carriers will be lost if the photon is absorbed closer to the electrode, as the cloud needs to expand less to intersect the electrode. This effect is evident for photon energies just above the carbon edge, where the photoelectric attenuation length is significantly less than 1 μm.

While this incomplete charge collection near the window layer may be likely to be due to recombination at the window electrode, we presently have insufficient information to model our results in detail with respect to this behavior. Fortunately, it appears quantitatively sufficient (within the error limits of the measurements and this scope of the present work) to treat this recombination region as effectively "dead" carbon and include it as part of the diode "window" in our responsivity model. Near the metal window electrode, where the field is insufficient to extract all the generated photocurrent, the diamond is effectively "dead" and does not contribute to the collected charge. The thickness of this "dead" layer of diamond as determined from fits to our experimental data is roughly 60 ± 30 nm as measured on several samples. We are presently pursuing a more detailed and quantitative investigation of this behavior and intend to report on it in a subsequent article.

The measured hole responsivity of one diamond sensor at energies ranging from 0.25 to 7.0 keV is shown in Fig. 5. The energy-dependent responsivity S is simply calculated as follows:

$$S = \frac{1}{W} T_{\text{window}}(1 - T_{\text{active}})$$

where W is the (energy-independent) mean electron-hole pair production energy, T_{window} is the X-ray transmission of the electrode (window layer), and T_{active} is the X-ray transmission of the active sensor material. The transmission values are readily calculated using variable material thickness and known X-ray optical data for the elements [29,30]. Material thicknesses are therefore determined from the magnitude of transmission edge drops in the energy scan, and W is determined from the overall magnitude of responsivity. Agreement of the experimental data with the "smooth" fitting function, even as the flux varies abruptly with optical configuration, indicates linearity of responsivity with flux in the 1 nW–10 μW/mm^2 range.

4. Conclusion

We have found that high quality single crystal synthetic diamond material with ultralow nitrogen content contains primarily electron traps (holes may be trapped as well, but are majority carrier for all of these measurements). With blocking contacts, hole transmission through 500 μm diamond of this type can be made to represent calculable and linear photodiode responsivity (with respect to duty cycle and incident power) under continuous illumination using a pulsed bias scheme. Pre-irradiation under zero field condition sufficient for carrier detrapping appears to be a requisite condition for reliable

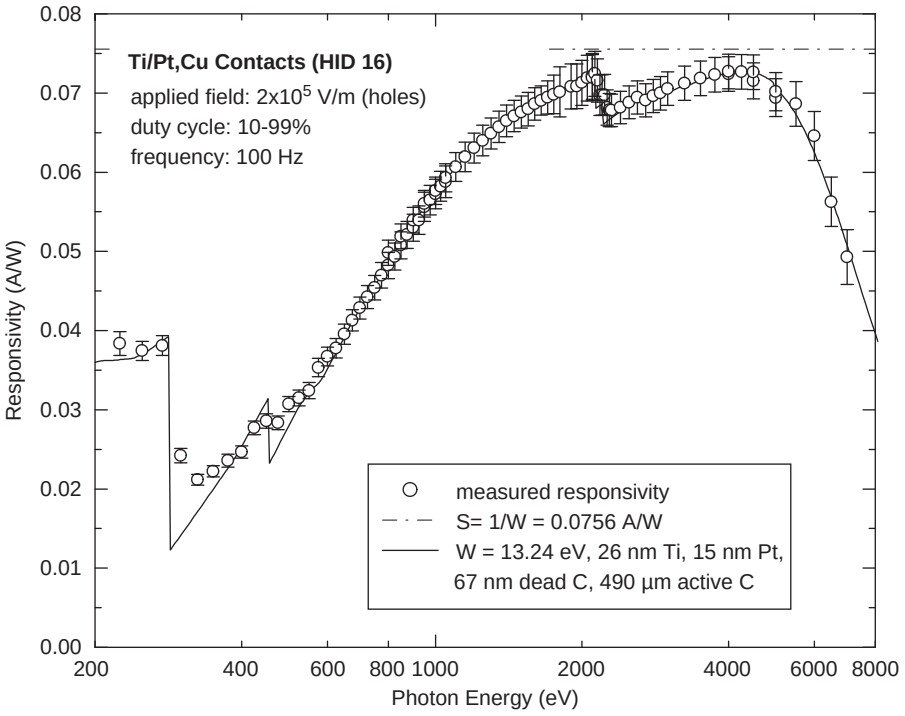

Fig. 5. Hole responsivity versus photon energy, measured over 0.25–7.0 keV, using 10–99% duty cycle, 100 Hz, and 100 V (0.2 MV/m) bias, for a 0.5 mm thick diamond with Pt-capped Ti incident contact and 25 nm Cu transmission contact.

instantaneous responsivity (possibly applicable for pulsed illumination application).

Methodology for performing DC radiometry with such a diamond photodiode was developed to allow the determination of physical values such as film thicknesses, as well as the mean electron–hole pair creation energy W for diamond. This work finds a value of 13.25 ± 0.5 eV for W. However, since we have seen that charge trapping and recombination can reduce the bulk responsivity of diamond with respect to both electron and hole transmission, we should emphasize that any such measurement is at best an upper bound.

At photon energies above 4 keV, the character of transmission through a 500-µm-thick diamond sample can no longer be considered purely "holes" (since photoabsorption takes place near the center of the sample). For this reason, lower duty cycle is prescribed for DC photocurrent measurements at higher energies.

Although we have exclusively used current-mode test methods in this work, the pulse structure we have characterized suggests that for applications in which single short pulses will be measured, charge trapping should not be a significant limitation to quantitative flux measurement, provided that detrapping is ensured or flux is relatively low.

Future work will include quantification of recombination and photoconductive gain effects.

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