Effects of γ-ray radiation on two-dimensional molybdenum disulfide (MoS2) nanomechanical resonators

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We report on experimental investigation and analysis of γ-ray radiation effects on two-dimensional molybdenum disulfide (MoS2) drumhead nanomechanical resonators vibrating at megahertz frequencies. Given calibrated dosages of γ-ray radiation of ~5000 photons with energy at 662 keV, upon exposure over 24 or 12 h, all the MoS2 resonators exhibit ~0.5–2.1% resonance frequency upshifts due to the ionizing γ-ray induced charges and their interactions. The devices show γ-ray photon responsivity of ~30–82 Hz/photon, with an intrinsic γ-ray sensitivity (limit of detection) estimated to approach ~0.02–0.05 photon. After exposure expires, resonance frequencies return to an ordinary tendency where the frequency variations are dominated by long-term drift. These γ-ray radiation induced frequency shifts are distinctive from those due to pressure variation or surface adsorption mechanisms. The measurements and analyses show that MoS2 resonators are robust yet sensitive to very low dosage γ-ray, demonstrating a potential for ultrasensitive detection and early alarm of radiation in the very low dosage regime. © 2016 AIP Publishing LLC.

Radiations such as energetic subatomic particles or photons generated from nuclear reactions1 have been exploited in a wide range of applications, from basic science (e.g., observing γ-ray bursts for studying cosmology2) to industry (e.g., electricity generation in nuclear plants) and nuclear medicine (e.g., imaging).3 Meanwhile, with sufficient energy, such radiations may damage matters by breaking atomic bonds, ionizing atoms, or causing harmful biomolecular effects in living tissues.3 To safely utilize radiations, it is desirable not only to develop various robust detectors capable of operating in harsh environments with high levels of radiations such as in nuclear reactors, but also to explore highly responsive and sensitive materials and devices for very early alarm of low dosage radiations or leakage. In all these scenarios, detection of ionizing radiations is of great importance for identifying, quantifying, and monitoring radiation sources and activities.

Historically gas-filled chambers have been the earliest for detecting ionizing radiations via the gas ionization. Since 1940s, scintillation crystals combined with photomultiplier tubes (PMT) have prevailed as the mainstream solutions in many applications to date. Later semiconductor junction devices have been extensively studied for compact pixel and array detectors.4,5 Among the various possible semiconductor device platforms and detection mechanisms for ionizing radiations, resonant micro/nanoelectromechanical systems (MEMS/NEMS) offer excellent promises and sustainable improvement with device scaling.6,7 In particular, because NEMS resonances are exceptionally responsive to variations in their modal masses and stiffnesses, considerable interests and efforts have been stimulated in exploiting nanoresonators for ultrasensitive detection of physical quantities such as mass and force, attaining yocto-gram (10^-21 g)8 and zepto-newton (10^-21 N)9 sensitivities. Responses of nanoresonators to radiations such as γ-ray particles, however, have not yet been reported.

Atomic layer crystals, such as graphene and molybdenum disulfide (MoS2), have emerged as advanced materials for 2D electronic,9,10 mechanical,11–15 and optical16 devices. Responses of graphene transistors to radiations have been recently investigated.17–19 In contrast to graphene as a semimetal,20 MoS2 is a semiconductor with bandgaps (BGs) near 1.3–1.9 eV, depending on its number of layers,21 and comparable with BGs of conventional semiconductor radiation detectors. Moreover, MoS2 possesses higher interaction probability (Eq. (1)) with γ-ray radiation than graphene does (given the same number of layers, down to monolayer limit), owing to its larger thickness per unit layer, and higher mass density (see Fig. 1(c)).

In this work, we explore effects of γ-ray radiation on multilayer MoS2 nanoresonators (Figs. 1(a) and 1(b)). We perform γ-ray irradiation using a 1mCi 137Cs source and monitor resonance responses of MoS2 nanoresonators to demonstrate the γ-ray radiation effects. We observe resonance upshifts in all devices upon irradiation, caused by ionizing γ-ray induced charging and charge-induced tensioning. Quantitative calculations with radiation dosage show that the MoS2 nanoresonators exhibit promise for sub-single γ-ray photon sensitivity.

MoS2 drumhead nanoresonators are fabricated by mechanical exfoliation onto lithographically patterned 290 nm-SiO2-on-Si substrate with circular microtrenches,11 with diameters d ≈ 5–6 μm and thicknesses from few-layer to thin film of t ≈ 30–80 nm. After exfoliation, MoS2 resonators are annealed at 300 °C for 3 h in vacuum to remove surface

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The probability of a photon interacting with the MoS2 drum-circular cylindrical detector is using a calibrated NaI scintillator. The radiation flux on the quantifies radiation exposure. The devices (see Fig. 1(c)). These calculations, however, neglect secondary interactions with the MoS2 nanoresonator, we employ three completely sealed MoS2 diaphragms and two partially covered drumheads with holes, which allow air flow in cavity. All measurements, including γ-ray irradiation and calculated interaction probability of photons and a MoS2 nanoresonator. (a) Aerial and (b) cross-sectional illustrations of γ-ray irradiation on a MoS2 resonator, demonstrating generations of secondary γ photons and fast electrons. (c) Calculated interaction probability of 662 keV γ-ray on MoS2 (red line) and Si (blue dashed line) and graphite (black dotted line). Blue colored regime indicates thickness of employed MoS2 resonators.

where is the isotope half-life time. For 662 keV137Cs, 1/2 the exposure time, and is the distance from source to detector. Since the intrinsic peak efficiency is unknown and depends on detector material, radiation energy, and detector thickness, we first calibrate the employed NaI detector. Detector peak efficiency can be separated into two components, where is the geometrical efficiency. In the case of an isotropic point source, geometrical efficiency is . Here, is the solid angle of the detector relative to the source position. If the source is located along the axis of a circular cylinder detector of radius , we have . The absolute source activity is where 662 keV is the photon emission probability. The detector peak efficiency for such geometry can be rewritten as

The source activity can be estimated at a particular time if its initial activity is known, where is the isotope half-life time. For 662 keV 137Cs, is 10 986 ± 33 days. By using a radiation source with a given activity and the photopeak counts, the detector photopeak efficiency, , can be plotted against the source-detector distance (Figs. 2(a) and 2(b)). From the fitting, we obtain intrinsic peak efficiency of where 662 keV (Fig. 2(c)) from ~1 mCi 137Cs source. We thus estimate that the flux 5 cm away from the source is .

After the careful calibration of dosage, we focus on measuring MoS2 resonance responses before and after radiation exposure. Immediately after annealing at 300 °C for 3 h in vacuum, thermomechanical resonances of MoS2 devices are adsorbates and restore the devices, and devices are promptly transferred into a vacuum chamber after annealing. Among fabricated resonators, we employ three completely sealed MoS2 diaphragms and two partially covered drumheads with holes, which allow air flow in cavity. All measurements, including γ-ray exposure and resonance, are performed in moderate vacuum (~20 mTorr) to eliminate measurable air damping.

We first estimate the interaction probability between a γ-ray photon and the MoS2 resonator. The probability of monoenergetic photons traveling through a medium of thickness without interaction is , where is the total linear attenuation coefficient mainly due to Compton scattering and photoelectric effect. The interaction probability is

where is total (Compton + photoelectric) mass attenuation coefficient per density, and is the mass thickness of the absorber (MoS2 here). As MoS2 is a compound, we have

where is the weight fraction of element (Mo, S). The calculated mass attenuation coefficients in MoS2 using Eq. (2) are summarized in Table I. With Eq. (1) and results in Table I, the probability of a photon interacting with the MoS2 drumhead is , depending on thickness of devices (see Fig. 1(c)). These calculations, however, neglect secondary γ-ray or fast electrons that may have been produced. Thus, the actual interaction rates with the MoS2 nanoresonators can be larger than the calculated values. Consider the ultrathin MoS2, most of the γ-ray photons interact with the ~550 μm-thick Si substrate (underneath the vibrating MoS2 resonators and the ~290 nm SiO2).

We then calibrate the incident photon flux on device to quantify radiation exposure. The γ-ray dosage is measured using a calibrated NaI scintillator. The radiation flux on the circular cylindrical detector is

\[
\Phi = \frac{N_p(L, E)}{S_{DTL} \varepsilon_e(E)},
\]

where is energy of γ-ray, is the scintillator detector’s effective surface area, is the number of events recorded in the photopake, is the exposure time, and is the distance from source to detector. Since the intrinsic peak efficiency is unknown and depends on detector material, radiation energy, and detector thickness, we first calibrate the employed NaI detector. Detector peak efficiency can be separated into two components, , where is the geometrical efficiency. In the case of an isotropic point source, geometrical efficiency is . Here, is the solid angle of the detector relative to the source position. If the source is located along the axis of a circular cylinder detector of radius , we have . The absolute source activity is where is the photon emission probability. The detector peak efficiency for such geometry can be rewritten as

\[
\varepsilon_p(L, E) = \frac{N_p(L, E)}{A_{DL} f_p(E)} = \frac{\varepsilon_e(L)}{2} \left( 1 - \frac{L}{\sqrt{L^2 + r^2}} \right).
\]

The source activity can be estimated at a particular time if its initial activity is known, where is the isotope half-life time. For 662 keV 137Cs, is 10 986 ± 33 days. By using a radiation source with a given activity and the photopeak counts, the detector photopeak efficiency, , can be plotted against the source-detector distance (Figs. 2(a) and 2(b)). From the fitting, we obtain intrinsic peak efficiency of where 662 keV (Fig. 2(c)) from ~1 mCi 137Cs source. We thus estimate that the flux 5 cm away from the source is .

After the careful calibration of dosage, we focus on measuring MoS2 resonance responses before and after radiation exposure. Immediately after annealing at 300 °C for 3 h in vacuum, thermomechanical resonances of MoS2 devices are

**Table I.** Photon mass attenuation coefficients (μ/ρ) of MoS2 due to different interaction mechanisms. The unit for the mass attenuation coefficients is [cm² g⁻¹].

<table>
<thead>
<tr>
<th>Eᵢ (keV)</th>
<th>Scattering</th>
<th>Pair production</th>
<th>Total attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coherent (Rayleigh)</td>
<td>Incoherent (Compton)</td>
<td>Photoelectric absorption</td>
</tr>
<tr>
<td>662</td>
<td>1.492 × 10⁻³</td>
<td>7.103 × 10⁻²</td>
<td>2.851 × 10⁻³</td>
</tr>
</tbody>
</table>
monitored without γ-ray exposure using a customized optical interferometry system sketched in Fig. 3(c). As shown in Figs. 4 and 5, resonances of the devices are in the range of ~15–21 MHz and gradually drift toward lower frequency over long time. This drift is attributed to slow adsorption of air molecules onto devices (inside moderate vacuum). After tracking resonances over 36 h (Figs. 5(a)–5(d)), we locate the ~1 mCi 137Cs sealed source ~5 cm away from the resonators, and expose the devices to 662 keV γ-ray radiation for ~24 h in vacuum (Fig. 3). During the radiation exposure period, each device is exposed to $N_{\text{total}} \approx 5000 \gamma$-ray photons at 662 keV, estimated from radiation flux upon given device area and exposure time. The number of photons interacting with MoS₂ devices is $N_{\text{MoS}_2} = N_{\text{total}} \times P_{\text{MoS}_2} \approx 0.01$ photon, suggesting that thin MoS₂ nanoresonators are mostly transparent for high energy γ-ray photons. After 24 h of exposure, the 137Cs source is removed, and the resonances are monitored again for ~60 h. Immediately after γ-ray exposure, all the resonators exhibit ~0.5–2.1% resonance frequency upshifts, which correspond to radiation responsivity ( $\delta f / N_{\text{total}}$ ) of $\delta f_{\text{total}} \approx 30$ to 82 Hz/photon. After that, resonances of all the devices return to their initial tendency of ordinary long-term drifting. Once resonances return to the drifting trend, they do not exhibit further noticeable frequency upshifts. For Device #5, we apply a shorter period (12 h) of γ-ray exposure, while measuring the resonance with much shorter intervals before and after exposure. The data in Fig. 5(e) clearly demonstrate the same signature of repeatable and robust frequency upshift.

Further, we estimate the intrinsic γ-ray radiation resonant sensitivity (limit of detection) of a MoS₂ nanoresonator by employing its intrinsic frequency stability. Frequency stability given by fractional frequency fluctuations over averaging time $\tau$ is

$$\frac{\Delta f}{f_0} \tau = \left( \frac{1}{Q} \right) \times \left( \frac{\pi k_B T}{P_c \tau} \right)^{1/2},$$

where $f_0$ is resonance frequency, $Q$ is quality factor, $k_B$ is Boltzmann constant, $T$ is temperature, and $\tau$ is averaging time. Here, $P_c = \pi f_0 k_B a_c^2 / Q$ is operating power of the resonator, $k_B$ is effective stiffness, and $a_c$ is displacement at critical point. For Device #1, the measured critical point response gives $a_c \approx 1.5$ nm, which yields $P_c \approx 3$ pW. At $T \approx 300$ K, estimated frequency stability of Device #1 with 1 s averaging time ($\tau = 1$ s) is $\langle \delta f_0 / f_0 \rangle_{\tau=1s} = 1.1 \times 10^{-7}$, and thus $\delta f_{\text{total}} \approx 0.2\%$. This stability level leads to a γ-ray radiation sensitivity of $\delta f / \delta N \approx 0.02$–0.05 photon for Devices #1–#5 ($\tau = 1$ s), showing deep sub-single γ-ray photon limit of detection. If we relax the frequency stability to a modest $2 \times 10^{-5}$, compromised by extrinsic noise and practically more achievable, this leads to γ-ray photon sensitivity of ~0.5–1 photon (for Devices #1–#5).

The observed resonance upshifts (in all devices) upon radiation exposure can be understood by examining charge generation in the device structure. Among reasons that may vary resonances, we can first exclude adsorption-induced frequency shifts where downshifts are expected due to added mass. In addition, we can also rule out frequency shifts associated with membrane bulging due to pressure change in sealed cavity, because devices with both sealed and leaking cavities exhibit the same frequency upshifts upon radiation. Hence, the most relevant mechanism of radiation effects on these resonators is generation and interaction of charges. Because we carefully anneal each device before any measurement (an established protocol for restoring the device), without radiation exposure, resonance frequency slowly drifts toward lower frequency, due to adsorption of air molecules over time (Fig. 6). During radiation exposure, the direct interaction probabilities of a γ-ray photon with the MoS₂ resonators are very
multi-interactions generate trapped charges in the device structure again and further create larger numbers of photons and fast electrons, which interact with the device structure across the SiO2 layer (Figs. 6(c) and 6(d)) and cause electrostatic forces between the charged MoS2 drumhead and the Si substrate, resulting in electrostatic tension and deflection of the MoS2 drumheads (Fig. 6(d)), and the resonance frequency upshifts. After exposure expires, trapped charges are neutralized over time, so that the resonance frequencies return to the initial frequency tendency (Fig. 6(e)). We note that the quantitative details of the charging mechanism of γ-ray interaction with the device structure may depend on the work function of the Si substrate. It could be interesting to alter and engineer the work function of the substrate by depositing different metals of interest, or forming metal silicides on the Si substrate, and investigate how the device resonance changes with the work function.

Furthermore, we estimate the tension and deflection induced in MoS2, based on the measured frequency upshifts. The resonance frequency of clamped circular drumhead resonators in this study can be determined by

\[
 f_0 = \frac{1}{2\pi} \left( \frac{k d}{2} \right) \left( \frac{16D}{\rho t d^4} \left[ \frac{k \rho d^2}{2} + \frac{\sigma t d^2}{4D} \right] \right)^{1/2}, \tag{6}
\]

where \( d \) is the diameter, \( t \) the thickness, \( D = E\gamma^2/[12(1 - \nu^2)] \) the bending rigidity, \( \sigma \) the tension [N/m²], \( E \gamma \) the Young’s modulus, \( \rho \) the density, and \( \nu \) the Poisson’s ratio of MoS2, and \( k \) is the mode parameter determined numerically.26 Extracted Young’s modulus of MoS2 from the resonances data is 0.2–0.4 TPa, showing good agreement with the previously reported values.13,27 For further analysis, we employ Device #1 which particularly does not consist of structural defects (e.g., thickness variation or holes) for modeling. The initial surface tension on MoS2 resonators is ~0.1 N/m (6.84 ppm of strain).13 Upon γ-ray exposure, the resonance frequency of Device #1 shifts from ~19.375 MHz to ~19.784 MHz, which yields a tension level of ~0.240 N/m (16.41 ppm of strain), corresponding to ~12 nm static displacement at the center of the diaphragm.

FIG. 6. Illustrations of γ-ray radiation effects on a MoS2 resonator. (a) Clean MoS2 resonator right after annealing. (b) Air molecules adsorbing on device surface. (c) γ-ray irradiation onto device, generating secondary γ-ray photons and fast electrons. (d) γ-ray irradiation described in (c) produces trapped charges, which causes electrostatic forces, tension, and deformation of the MoS2 resonator. (e) Generated trapped charges are neutralized over time after radiation expires.

small, \( P_{MoS2} \approx 1.5 - 3.1 \times 10^{-6} \) (from Eqs. (1) and (2), Fig. 1(c)), because of the very thin devices, thus most γ-ray photons first strike the much thicker SiO2/Si substrate underneath the vibrating MoS2, producing secondary γ-ray photons and fast electrons, which interact with the device structure again and further create larger numbers of photons and secondary electrons (SE) (Fig. 6(c)). These cascade multi-interactions generate trapped charges in the device structure.
In conclusion, we have examined 662 keV γ-ray radiation effects from 1mCi $^{137}$Cs source upon 2D MoS$_2$ nanomechanical resonators. Our results show that MoS$_2$ nanoresonators offer excellent γ-ray radiation sensitivity, which would be particularly relevant in environments where radiation dosage is very low and early detection and alarm are desired. In addition, their small device footprints promise integration of MoS$_2$ resonators on chip, suggesting the possibilities for enabling compact and portable radiation detectors.

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