

# High density nitrogen-vacancy sensing surface created via He<sup>+</sup> ion implantation of <sup>12</sup>C diamond

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We present a promising method for creating high-density ensembles of nitrogen-vacancy centers with narrow spin-resonances for high-sensitivity magnetic imaging. Practically, narrow spin-resonance linewidths substantially reduce the optical and RF power requirements for ensemble-based sensing. The method combines isotope purified diamond growth, *in situ* nitrogen doping, and helium ion implantation to realize a 100 nm-thick sensing surface. The obtained 10<sup>17</sup> cm<sup>-3</sup> nitrogen-vacancy density is only a factor of 10 less than the highest densities reported to date, with an observed 200 kHz spin resonance linewidth over 10 times narrower. *Published by AIP Publishing.*

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The nitrogen-vacancy (NV) center in diamond is a versatile room-temperature magnetic sensor which can operate in a wide variety of modalities, from nanometer-scale imaging with single centers<sup>1,2</sup> to sub-picotesla sensitivities using ensembles.<sup>3</sup> Ensemble-based magnetic imaging, utilizing a two-dimensional array of NV centers,<sup>4-6</sup> combines relatively high spatial resolution with high magnetic sensitivity. These surfaces are ideal for imaging applications ranging from detecting magnetically tagged biological specimens<sup>7,8</sup> to fundamental studies of magnetic thin films.<sup>9</sup> A key challenge for array-based sensors is creating a high density of NV centers while still preserving the desirable NV spin properties. Here, we report on a promising method which combines isotope purified diamond growth, *in situ* nitrogen (N) doping, and helium ion implantation. In the 100 nm-thick sensor layer, we realize an NV density of 10<sup>17</sup> cm<sup>-3</sup> with a 200 kHz magnetic resonance linewidth. This corresponds to a DC magnetic sensitivity ranging from 170 nT (current experimental conditions) to 14 nT (optimized experimental conditions) for a 1 μm<sup>2</sup> pixel and 1 s measurement time.

Magnetic sensing utilizing NV centers is based on optically detected magnetic resonance (ODMR).<sup>10-12</sup> In the ideal shot-noise limit, the DC magnetic sensitivity is given by Ref. 9

$$\delta B_{\text{ideal}} \simeq \frac{h}{g\mu_B} \frac{1}{C} \frac{1}{\sqrt{\eta}} \sqrt{\frac{\delta\nu/\pi}{n_{\text{NV}}Vt}}, \quad (1)$$

in which  $h/g\mu_B = 36 \mu\text{T}/\text{MHz}$ ,  $C$  is the resonance dip contrast,  $\eta$  is the photon collection efficiency,  $\delta\nu$  is the full-width

at half maximum resonance linewidth,  $n_{\text{NV}}$  is the density of NV centers in imaging pixel volume  $V$ , and  $t$  is the measurement time. From Eq. (1), it is apparent that to minimize  $\delta B_{\text{ideal}}$  for a given linewidth  $\delta\nu$ , one would like to maximize the NV density  $n_{\text{NV}}$ . Increasing  $n_{\text{NV}}$ , however, can also increase  $\delta\nu$ . For example, lattice damage during the NV creation process can create inhomogeneous strain-fields.<sup>13</sup> More fundamentally, eventually NV-NV and NV-N dipolar interactions will contribute to line broadening. This dipolar broadening,  $\delta\nu_{dp}$ , is proportional to the nitrogen density  $n_N$ .<sup>14,15</sup> Since  $n_{\text{NV}}$  is typically proportional to  $n_N$ , we can divide  $\delta\nu$  into two components,  $\delta\nu = \delta\nu_0 + \delta\nu_{dp} = \delta\nu_0 + An_{\text{NV}}$ , to obtain

$$\delta B_{\text{ideal}} \simeq \frac{h}{g\mu_B} \frac{1}{C} \frac{1}{\sqrt{\eta V t \pi}} \sqrt{\frac{\delta\nu_0}{n_{\text{NV}}} + A}, \quad (2)$$

in which  $\delta\nu_0$  depends on factors independent of NV density (e.g., hyperfine interaction with lattice nuclei, inhomogeneous strain fields). The second term  $A$  is due to the dipolar contribution to the linewidth and will depend on the ratio of  $n_N$  to  $n_{\text{NV}}$ . Equation (2) implies that the magnetic sensitivity improves significantly with density until  $\delta\nu$  is dipolar limited. Thus, there is a threshold on the optimal NV density,  $n_{\text{NV}} \gtrsim \delta\nu_0/A$ .

There are practical reasons why, in the dipolar-broadened limit, it is beneficial to work at lower densities. By minimizing the ODMR linewidth, we minimize both the optical excitation (linear scaling with  $\delta\nu$ ) and radio frequency (RF) power (quadratic scaling with  $\delta\nu$ ) requirements for the measurement.<sup>16</sup> Additionally, reduced densities result in reduced photon count rates which maximize the measurement duty cycle, minimizing detector dead time/readout time. Thus, a

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reasonable method to optimize  $\delta B$  is to first minimize  $\delta\nu_0$  and then increase  $n_{NV}$  until the density independent and dipolar contributions to the sensitivity become comparable.

To minimize  $\delta\nu_0$ , this work utilizes nitrogen that is incorporated *in situ* during diamond growth via chemical vapor deposition (CVD) on a (100)-oriented electronic grade substrate (Element Six,  $n_{N,substrate} < 1$  ppb). *In situ* doping theoretically enables uniform-in-depth nitrogen incorporation in the 100 nm thick sensor while avoiding lattice damage caused by (more standard) nitrogen ion implantation. Additionally, we utilize isotopically purified  $^{12}\text{C}$  to eliminate  $\delta\nu$  broadening due to the NV hyperfine coupling to  $^{13}\text{C}$ .<sup>17,18</sup>

Next, the sample was implanted with  $\text{He}^+$  ions in arrays of  $5 \times 5 \mu\text{m}$  squares to create lattice vacancies. Different implantation conditions were tested with ion doses ranging from  $10^9$ – $10^{13} \text{cm}^{-2}$  at acceleration voltages of 15, 25, and 35 keV. After implanting, the sample was annealed at  $850^\circ\text{C}$  for 1.5 h in an  $\text{Ar}/\text{H}_2$  forming gas to allow the vacancies to diffuse to the doped nitrogen to form NV centers. A second 24 h anneal at  $450^\circ\text{C}$  in air was performed to convert NV centers from the neutral ( $\text{NV}^0$ ) to the negative ( $\text{NV}^-$ ) charge state.<sup>19</sup>  $\text{He}^+$  implantation into a uniformly N-doped layer, followed by annealing, produces a uniform layer of NV centers with a controllable sensor thickness. The method also provides independent handles on both nitrogen and vacancy densities to optimize NV formation. This is impossible with  $\text{N}^+$  implantation alone where typically dozens of vacancies are created for every implanted  $\text{N}^+$  ion.

To characterize the  $\text{NV}^-$  density, photoluminescence (PL) intensity from the  $\text{He}^+$  implanted squares was compared to an average of single, near-surface NV centers in a control sample. The 2D density was calculated with the known excitation spot size and converted to a 3D density by assuming a uniform distribution of NV centers throughout the 100 nm thick N-doped layer. As only the negatively charged state of the NV center is useful for magnetic sensing, room temperature PL spectra were used to confirm the synthesized centers were in the desired charge state.

Before  $\text{He}^+$  implanting and annealing, the density of NV centers formed during growth was in the range of  $0.7$ – $3 \times 10^{15} \text{cm}^{-3}$  (average value  $1.5 \times 10^{15} \text{cm}^{-3}$ ). The range in density is due to uneven incorporation of nitrogen during CVD growth which will be discussed further below. Figure 1 shows an  $\text{NV}^-$  density map, after annealing, of three squares implanted with  $10^{11}$ ,  $10^{12}$ , and  $10^{13} \text{cm}^{-2}$   $\text{He}^+$  ions at 15 keV. Experimentally we found that  $n_{NV}$  for the three acceleration voltages varied by less than a factor of 2. This is consistent with simulations<sup>20</sup> which show an average number of vacancies produced per ion of 30, 36, and 39, and an average ion range of 72, 112, and 135 nm, for 15, 25, and 35 keV acceleration voltages, respectively. All stopping ranges are within the 200 nm vacancy diffusion length<sup>21</sup> of the 100 nm N-doped layer.

During the implantation process, the entire sample was exposed to an unknown  $\text{He}^+$  radiation dose resulting in a background NV concentration of  $0.1$ – $1 \times 10^{16} \text{cm}^{-3}$ . Squares implanted with ion doses of  $10^9$  and  $10^{10} \text{cm}^{-2}$  were indistinguishable from this background in most of the implanted areas. The optimal ion dose was  $10^{12} \text{cm}^{-2}$  resulting in an average  $n_{NV}$  of  $1 \times 10^{17} \text{cm}^{-3}$  which corresponds to a 60-fold

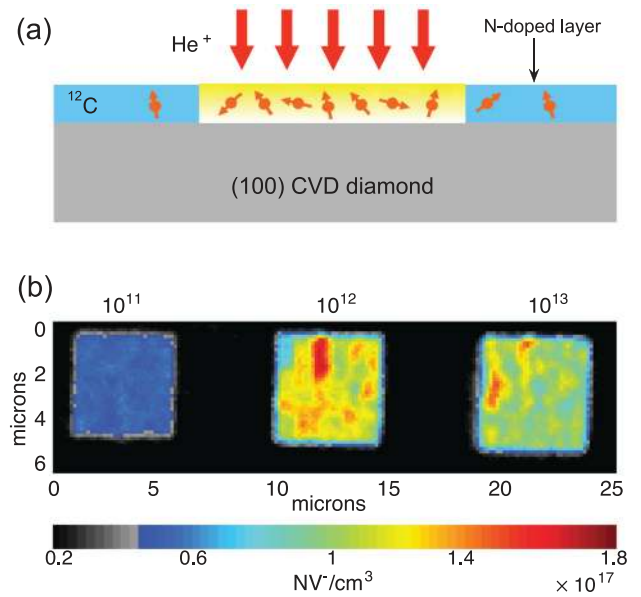


FIG. 1. (a) Schematic of the diamond sample illustrating the 100 nm  $^{12}\text{C}$  isotopically pure layer implanted with  $\text{He}^+$  ions. (b) Confocal scan of  $(5 \mu\text{m})^2$  implanted squares. Excitation at 532 nm with 1 mW power, collection band from 650 to 800 nm. From left to right, the squares were implanted with ion doses of  $10^{11}$ ,  $10^{12}$ , and  $10^{13} \text{cm}^{-2}$  at an acceleration voltage of 15 keV.

increase in  $n_{NV}$  over the unimplanted case. The obtained density is only one order of magnitude lower than the highest densities reported.<sup>11,22</sup> These very high densities were obtained in high nitrogen doped ( $>100$  ppm) diamond which exhibits significantly broader resonance lines (2 MHz),<sup>11</sup> where the dominant contribution is due to N-NV dipolar coupling.<sup>16</sup> Densities of  $10^{17} \text{cm}^{-3}$  have also been obtained with N implantation and annealing<sup>23</sup> which also exhibited several MHz linewidths.

Room-temperature spectra comparing the  $\text{NV}^-$  zero-phonon-line photoluminescence intensities for the implanted and unimplanted cases show a similar increase ( $\sim 40$ -fold) in NV density for the optimal implantation dose, as shown in Fig. 2(a). Figure 2(b) shows the ratio of  $\text{NV}^-$  to total NV ( $\text{NV}^- + \text{NV}^0$ ) for different optical powers. The high ratio at low intensities indicates the NV centers are predominately in the desired charge state in the absence of optical excitation. The decrease in ratio with increased power is consistent with photoionization effects reported previously.<sup>24</sup>

Next, we measured the ODMR linewidth,  $\delta\nu$ , of the doped layer. Figure 3(a) shows an (ODMR) spectrum for the  $m_s = 0 \leftrightarrow m_s = -1$  transition for one of the four NV crystal orientations. During the measurement, the NV centers are excited using a 532 nm continuous-wave (CW) laser, while an RF field is swept through the electron spin resonance. Three dips are observed due to the hyperfine interaction of the NV electronic state with the  $^{14}\text{N}$  nucleus.<sup>11</sup> To determine  $\delta\nu$ , the ODMR fluorescence spectra were fit to the sum of three Lorentzian functions of equal amplitude and  $\delta\nu$ , with a fixed 2.17 MHz hyperfine splitting.

Figure 3(b) shows a plot of  $\delta\nu$  vs. microwave power for the unimplanted and implanted conditions ( $15 \text{keV}$ ,  $10^{12} \text{cm}^{-2}$ ). The data are fit to the theoretical model  $\delta\nu = \delta\nu_{RF=0} + b\sqrt{P_{RF}}$ , where  $\delta\nu_{RF=0}$  is the intrinsic dephasing rate,  $P_{RF}$  is the applied RF power, and  $b$  is a constant scaling

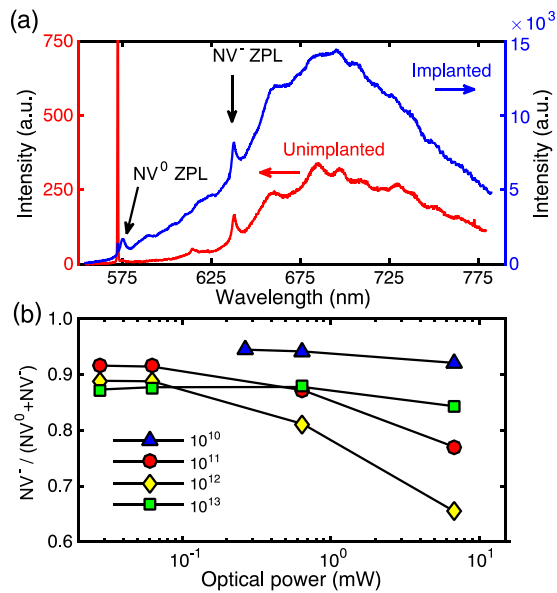


FIG. 2. (a) Spectra of unimplanted and implanted conditions illustrating the increase in photoluminescence after  $\text{He}^+$  implanting ( $15 \text{ keV}$ ,  $10^{12} \text{ cm}^{-2}$ ). Excitation at  $532 \text{ nm}$  with  $1 \text{ mW}$  power. (b) Plot of the ratio of  $\text{NV}^-$  to total NV vs. optical power. For the ratio, the difference in the relative weight of the  $\text{NV}^0$  and  $\text{NV}^-$  ZPL due to the different Huang-Rhys factors (approximately a factor of 2) has been taken into account.<sup>25,26</sup>

to account for RF power broadening. The inhomogeneous spin relaxation time,  $T_2^* = 1/(\pi\delta\nu_{RF=0})$ , is determined from this fit. Experimentally we found that optical excitation powers below  $100 \mu\text{W}$  did not affect  $T_2^*$ . No measurable difference in  $T_2^*$  was found between the unimplanted and  $15 \text{ keV}$  implantation cases, which both exhibit  $T_2^*$  of  $1.5 \mu\text{s}$  ( $\delta\nu \cong 200 \text{ kHz}$ ). As little improvement in NV density was observed for higher implantation energies, detailed  $T_2^*$  data for implantation energies greater than  $15 \text{ keV}$  were not taken.

The observed  $200 \text{ kHz}$  linewidth for our dense ensemble of NV centers is similar to ensembles created via electron irradiation of  $1 \text{ ppm}$  N bulk  $^{12}\text{C}$  diamond,<sup>27</sup> and 2–5 times narrower than naturally abundant diamond.<sup>11,28</sup> This suggests that there is a significant benefit in utilizing isotope purified  $^{12}\text{C}$  for  $\text{He}^+$  implanted samples. The  $200 \text{ kHz}$  linewidth is significantly broader than the  $10 \text{ kHz}$  inhomogeneous linewidth demonstrated in low-nitrogen  $^{12}\text{C}$  diamond,<sup>29</sup> which was limited by variations in the microscopic strain in the sample.<sup>9</sup> Given the minimal difference in  $T_2^*$  for unimplanted vs. implanted conditions, we attribute the dominant dephasing mechanism to dipolar interactions between the NV centers and native nitrogen.

A critical parameter which affects magnetometry performance is the ratio of  $n_{\text{NV}}$  to the density of all other paramagnetic impurities. Assuming the latter is dominated by unconverted substitutional nitrogen, then the relevant quantity is  $n_{\text{NV}}/(n_{\text{N}+\text{NV}})$ . We can estimate this ratio using two different methods. First, for CVD diamond grown on a (100) substrate, the initial ratio of  $n_{\text{N}} : n_{\text{NV}}$  is typically found to be  $100 : (0.2\text{--}0.5)$ .<sup>30</sup> After helium ion implantation and annealing, the NV density increased by 40–60 times, suggesting that  $n_{\text{NV}}/(n_{\text{N}+\text{NV}})$  ranges from 8% to 30%. Alternatively, we can directly use the ESR linewidth. We again assume the dominant contribution to the linewidth is the dipolar coupling

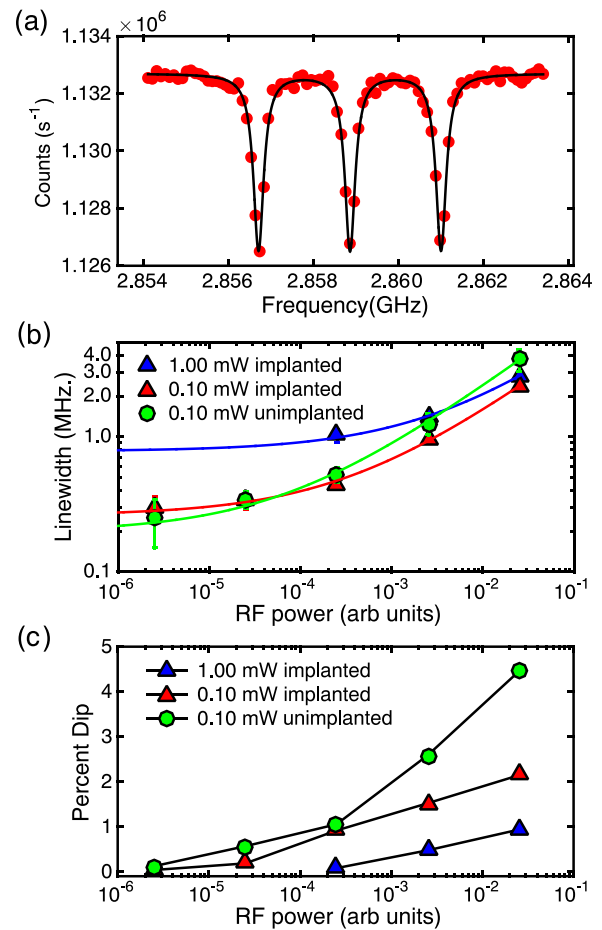


FIG. 3. (a) ODMR scan of an implanted square with  $\delta\nu = 290 \text{ kHz}$  excited with  $78 \mu\text{W}/\mu\text{m}^2$  of optical power. (b) Measured linewidth ( $\delta\nu$ ) vs. RF power. The error bars signify the 95% confidence interval of the width parameter for the Lorentzian fit function. (c) Optical contrast (depth of the resonance dip) vs. microwave power for unimplanted and implanted ( $15 \text{ keV}$ ,  $10^{12} \text{ cm}^{-2}$ ) conditions.

between the NV and substitutional nitrogen. The ESR linewidth of the spin 1/2 substitutional nitrogen interacting with the nitrogen bath is known to be  $\delta\nu = 3.1 \times 10^4 f_{\text{N}}$  (Hz/ppm),<sup>14</sup> where  $f_{\text{N}}$  is the nitrogen concentration in ppm. Given the similar gyromagnetic ratio for N and NV, we can use this experimental linewidth to estimate the linewidth of an NV center interacting with a N bath. This results in  $f_{\text{N}} = 6.4 \text{ ppm}$  for a  $200 \text{ kHz}$  linewidth and  $n_{\text{NV}}/(n_{\text{N}+\text{NV}}) = 8\%$  which is consistent with the former estimate.

We now estimate the DC magnetic sensitivity of the engineered layer for a  $1 \text{ s}$  integration time. For a sensor biased at the steepest slope of the ODMR curve, the shot-noise magnetic sensitivity is given by<sup>9</sup>

$$\delta B_{\text{sn,cw}} \simeq \frac{h}{g\mu_B} \frac{1}{C} \frac{\delta\nu}{\sqrt{I_0 t}}, \quad (3)$$

in which  $I_0$  is the detected photon count rate from the NV centers in the measurement pixel. For the case of continuous-wave (CW) RF and optical fields, the realized sensitivity is a complex interplay between optical and RF power. The optical excitation power has counteracting effects on  $\delta B_{\text{sn,cw}}$ , both increasing  $I_0$  and, typically,  $\delta\nu$  (Fig. 3(b)). Similarly, increasing the RF power will both increase  $\delta\nu$  and  $C$  (Fig. 3(c)). For

a  $1\ \mu\text{m}^2$  pixel, we find a sensitivity of  $\delta B_{\text{sn,cw}} \simeq 170\ \text{nT}$  at  $100\ \mu\text{W}$  optical excitation power and an RF power corresponding to  $C=0.01$ . This can be readily improved by a factor of  $\sqrt{3}$  utilizing a high-NA objective<sup>31</sup> and a further factor of 3 by driving all three hyperfine transitions simultaneously, resulting in a sensitivity of  $\delta B_{\text{sn,cw}} \simeq 30\ \text{nT}$ .

The sensitivity can be further improved utilizing pulsed techniques. In this case, we can decouple the optical excitation from the spin manipulation, enabling the use of high optical powers for spin readout without adversely affecting the ODMR linewidth. The optimal spin-manipulation time is  $\approx T_2^*$ ,<sup>15</sup> resulting in a time-averaged photon count rate of  $I_0 \rightarrow I_0 \tau_L / (T_2^* + \tau_{\text{init}} + \tau_L)$  in Eq. (3), in which  $\tau_L$  is the optical read-out pulse length and  $\tau_{\text{init}}$  is the initialization time.<sup>9</sup> The pulsed sensitivity is given by

$$\delta B_{\text{sn,pulsed}} \simeq \frac{h}{g\mu_B C} \frac{\delta\nu \sqrt{1/\pi\delta\nu + \tau_{\text{init}} + \tau_L}}{\sqrt{I_0 \tau_L t}}, \quad (4)$$

which reduces to Eq. (1) in the limit that  $T_2^* \gg (\tau_{\text{init}} + \tau_L)$ . Using reasonable parameters ( $\tau_L = 300\ \text{ns}$ ,  $\tau_{\text{init}} = 1\ \mu\text{s}$ ,  $C = 0.05$ ,  $I_0 = n_{\text{NV}} V \times 10^5\ \text{counts s}^{-1}$  (Ref. 31)), we estimate a sensitivity of  $\delta B_{\text{sn,pulsed}} \simeq 14\ \text{nT}$ . We note that most ensembles experiments work in the regime in which  $T_2^* \ll (\tau_{\text{init}} + \tau_L)$  which results in  $\delta B \propto (T_2^* \sqrt{I_0})^{-1} \propto \sqrt{1/T_2^*} \propto \sqrt{n_{\text{NV}}}$ . In this duty-cycle limited regime, it is still advantageous to increase  $T_2^*$  even in the dipolar-broadened limit. By raising  $T_2^*$  to  $1.5\ \mu\text{s}$ , which is comparable to typical choices for  $(\tau_{\text{init}} + \tau_L)$ , we make significant step toward suppressing this duty cycle issue and reaching the fundamental ensemble DC sensitivity.

In future sensors, optimizing the initial nitrogen density  $n_N$  such that  $\delta\nu_0 \approx \delta\nu_{\text{dp}} \approx 10\ \text{kHz}$  could result in a further  $\sim 10$ -fold decrease in the ODMR linewidth. More critically, however, is the need to further improve the uniformity of N incorporation during CVD growth. In this work, initial nitrogen incorporation densities varied by a factor of 3–4. Theoretically, in a calibrated, stable imaging system, this deviation should not pose a problem. Practically, however, spatial variations over time (e.g., due to vibrations or thermal drift) will result in a false magnetic signal. It has been recognized that nitrogen incorporation during diamond growth is extremely sensitive to the growth plane<sup>32,33</sup> and thus surface steps on a (100) surface. By reducing the misorientation of the surface cut (typically 1% in our samples), we expect to be able to enhance the incorporation homogeneity. High NV spatial uniformity combined with the realized optical and spin properties presented in this work is expected to result in a high-sensitivity magnetic imaging system for magnetically tagged biological applications and the study of optical-scale magnetic phenomena.

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