Ultralow Superharmonic Resonance for Functional Nanowires

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ABSTRACT Functional nanowires, made from materials such as zinc oxide, offer the promise of energy scavenging and precise sensing due to their vibrational properties, but their high intrinsic resonance frequencies (in the kilohertz to megahertz range) have limited the applications in nanotechnology. In this paper, we describe a method for introducing a new type of resonance at ultralow frequencies in ZnO nanowires. By using in situ ion implantation, nanodevice assembly, electronic signal generation, mechanical measurement, and electron beam characterization, we have achieved resonance at frequencies two orders of magnitude lower than the natural resonance frequency. Through both experimental investigation and theoretical simulation, we show that electric charge imbalance arising from focused ion beam exposure is responsible for the creation of this unprecedented superharmonic resonance behavior in ZnO nanowires.

KEYWORDS Nanowires, resonance, sensors, energy harvesting, power generating

n recent years, functional nanowires have been extensively studied for their potential as ultraprecise sensors,^{1,2} actuators,³ balances,^{4,5} as well as energy-scavenging devices.⁶ By fixing nanowires as cantilevers and exploiting their vibrational properties, it has been possible to develop applications as diverse as electric components that can selfpower using body movements or biosensors that can detect the presence of individual molecules based on their vibrational properties.^{7,8} However, many of the most exciting applications of vibrating nanowires have faced an important roadblock: the resonance frequency of nanowires is typically in the kilohertz to megahertz range, while the driving frequencies involved in sensing and energy-scavenging applications are several orders of magnitude lower. Therefore, it is crucial to find solutions to lower the frequency range in which nanowires can resonate.⁸ Here we report a novel method that allows nanowires of materials such as zinc oxide (ZnO) driven by an oscillating electric field to experience resonance at low fractions of their natural frequency by means of ion implantation. Using this technique, we are able to selectively tune ZnO nanowires in order to make them sensitive to frequency ranges as low as 1/66 of their natural resonance frequency. These ultralow superharmonic frequencies could therefore offer tremendous advances in the field of nanosensors and self-powered devices, and open an avenue for low-frequency applications as well as selective frequency tuning

We have configured ZnO nanowires as cantilevers by attaching one end to a nanoelectrode and leaving the other free in a scanning electron microscope (SEM). The nanowires are driven to vibrate by an oscillating electric field between the substrate nanoelectrode and a second nanoelectrode positioned above the nanowire. The large dc component in the field brings free charge to the tip of the nanowire, and as long as the nanowire's equilibrium position is not parallel to the electric field, the transverse component of the oscillating electric field dominates. In this case, the vibrational response of the nanowire as a function of the driving frequency, Ω , closely follows the classical behavior predicted by the Euler–Bernoulli model for elastic rods. The appearance of resonances is classically dictated by the Euler equation

$$-YI\frac{\partial^4 U(x,t)}{\partial x^4} + f(x,t) = \rho A \frac{\partial^2 U(x,t)}{\partial t^2}$$
(1)

where U(x) is the deflection from the equilibrium axis at position *x* along the nanowire, *Y* is the elasticity (or Young's modulus), ρA is the mass per unit length, *I* is the area moment of inertia, and f(x,t) is the externally applied force. Supplemented with the appropriate boundary conditions, this system leads to a natural resonance frequency $\omega_0 = 1.876^2(YI/\rho A)^{1/2}$, as well a second harmonic mode at $6.2\omega_0$. In the classical case the nanowire does not enter resonance below these frequencies.

One exception has been reported in which nanowires can be made to resonate at an integer fraction of their natural frequency when driven by a parametric driving force. Yu et al. observed the appearance of parametric resonance up to fourth order $(2\omega_0/n, n = 1, 2, 3, 4)$ in a boron nanowire, and this led to a new interest in the phenomenon of parametric resonance as a way to sensitize nanowires to lower resonance frequencies.⁹ However, the search for ultralow resonance frequencies was largely discontinued because the existing mechanism could only enable parametric resonance up to a relatively low order ($n \le 4$). In this paper, we describe a new approach that utilizes charge imbalance in nanowires in order to bring parametric resonance to a higher order of n > 130.

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FIGURE 1. Schematic diagram of the experimental setup. The setup is comprised of a pair of needle-shaped nanoprobes configured as electrodes via an electrical circuit, with a ZnO nanowire fixed to the anode and placed about 5 μm away from the cathode. The electric field between the two electrodes consists of a sinusoidal ac field superimposed onto a constant dc field. After one face of the nanowire is exposed to a focused ion beam system, the nanowire enters resonance for ac frequencies smaller than its natural frequency.

We first present the experimental methods which were employed to sensitize ZnO nanowires by ion beam exposure and to subsequently measure their resonance frequencies. Next, we describe the material effects of ion exposure on a ZnO nanowire, including the change in local elasticity and the accumulation of electric charge imbalance. Using these results, we then present a resonance model indicating how electric charge imbalance can induce the observed ultralow harmonic resonance.

Experimental Methods. Wurtzite ZnO nanowires were synthesized using thermal evaporation of oxide powders without the presence of a catalyst. ZnO powders of 99.99% purity were heated in a tube furnace until they evaporated, then the resulting nanostructures were captured on a plate at the downstream end of the furnace. The resulting nanowires were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). They were found to be monocrystalline, wurtzite nanowires with diameters ranging from 50 to 300 nm and lengths from 5 to 100 μ m. The nanowires were largely free of lattice defects and had only a thin layer of surface oxide from exposure to air. No particles were observed at the ends of the nanowires.

The nanowires were suspended in acetone and deposited onto a carbon-coated copper TEM grid before being mounted in the instrument for analysis. SEM characterization and in situ electromechanical measurements were carried out within a dual-beam focused ion beam (FIB) system (FEI DB Strata 235 FIB/SEM) equipped with a gas injection system for Pt deposition, a Zyvex F100 nanomanipulator system to manipulate the nanowires, and a Keithley 4200 nanoelectronic system for signal generation and measurement.

The nanowires were mounted into the final experimental setup, which was comprised of a pair of needle-shaped nanoprobes configured as electrodes via an electrical circuit, as shown in Figure 1. Each nanowire was successively fixed to the anode at an angle of approximately 15° from the plane of the anode, and the cathode was placed 5 μ m away from the tip of the nanowire. In order to assemble the

experimental setup, the nanowires were lifted from the grid using chemically sharpened tungsten nanoprobes, and Pt electrodes were deposited on the nanowire/nanoprobe junction to create mechanical and electrical connections. These electrodes were created by first injecting a cloud of organometallic molecules containing platinum ((MeCp)PtMe₃). The focused ion beam was then used to separate the platinum atoms from the organometallic precursor and deposit them on the junction in a layer approximately 1 μ m thick, using a beam current of 10 pA. A dc voltage with amplitude between 5 and 10 V was applied to the second electrode, and a sinewave ac voltage of between 0.5 and 1 V was applied to the nanowire using an Agilent 33220A function/arbitrary waveform generator. The frequency of the ac voltage was varied between 1 kHz and 2 MHz and the resulting amplitude of oscillation was observed via SEM. Length and diameter were measured by observing the dimensions of the nanowire at rest on the substrate grid. The nanoprobes were carefully coplanarized immediately before the experiment to prevent the extraplanar electric field from distorting the oscillations.

For a pristine, freshly attached nanowire, the frequency of the ac current was adjusted until the primary resonant frequency was found. The process of identifying the primary resonant frequency is described in further detail below. The nanowires were then exposed to a FIB beam, introducing defects in their structure. A Ga⁺ ion beam current of 100 pA at an accelerating voltage of 30 kV was used, and each individual nanowire received 30 s of constant exposure along its entire length. The exposure was produced by scanning the ion beam in a serpentine pattern over a square region containing the nanowire and the tungsten probe tip. Initially the vibration response was tested every 2 s; it was found however that a single continuous 30 s of exposure produced the most reproducible results with the least scanning time. The presence of defects was confirmed by TEM observation of nanowires after FIB exposure.

Experimental Results and Discussion. We now consider the resonance frequencies of a specific nanowire, whose behavior fell within the average of the nanowires observed in this study. The dimensions of this nanowire were 200 nm in thickness and 40 μ m in length. Prior to ion beam exposure, the natural resonance frequency of the nanowire was identified as the second lowest resonant frequency, since the electrically driven external force on the nanowire contains terms in both $sin(\Omega t)$ and $sin(2\Omega t)$ as has been discussed elsewhere.¹⁰ Above this frequency, the second harmonic was observed at approximately 6.2 times the primary resonant frequency, as expected for a classical oscillating cantilever. Using this standard methodology, we obtained a natural frequency $f_0 = 2\pi\omega_0 = 198$ kHz. Figure 2 shows the primary resonance and the second harmonic as observed using scanning electron microscopy imaging. No additional resonances were present between the primary frequency and the second harmonic, except for a duplicate resonance very near the natural frequency. This period

853



FIGURE 2. Scanning electron microscopy images showing the natural (a) and second harmonic (b) resonant modes of a ZnO nanowire driven by an oscillating electric field. The inserts in (a) and (b) illustrate the corresponding theoretical modes for a string fixed with both ends.

doubling is due to the fact that the ZnO nanowires used in this experiment had a rectangular cross section, which led to two distinct orientations of vibration for each classical mode. The period doubling thus corresponds to a vibration mode which is orthogonal to the plane of the first resonance and whose value depends on the specific cross-sectional morphology of the nanostructure. After FIB exposure, the natural resonance frequency remains unaltered (within a range of $\pm 10\%$), but a series of superharmonic resonances below ω_0 begin to appear. Each of these resonant vibrations is captured in a SEM image as shown in Figure 3, which clearly reveals a trend of increase in vibration amplitude. The vibrational behavior summarized in Table 1 indicates that after ion beam exposure, the superharmonic resonance frequencies of the ZnO nanowire vary inversely with the frequency number n. There is an excellent agreement between the observed resonance frequencies and calculated values according to the formula $\omega_n = 2\omega_0/2$ n, with a percent error consistently below 0.3%, as shown in Figure 4. This frequency pattern corresponds to the phenomenon of superharmonic resonance arising from parametric driving (parametric resonance has been studied extensively in the field of applied mathematics; see ref 11 for a valuable review of the topic). We were able to observe the appearance of superharmonic frequencies from n = 2 to n = 132, according to the sequence n = 2, 4, 12, 20, ..., 4(2m + 1), ending with a resonance at f_{min} = 2.98 kHz which corresponds to 1/66 of the natural frequency (or equivalently, n = 132).

In addition, the classical resonant modes—including the fundamental mode at ω_0 and the second harmonic at $\omega_1 \approx 6.2\omega_0$ —were each observed to occur at two different values which were very close to each other. This is consistent with the period doubling observed before ion beam exposure. In contrast, no period doubling was seen in the case of the superharmonic resonances. This absence indicates that the mechanism behind parametric resonance is "frozen in" to one orientation of the nanowire, thereby ruling out the possibility that the superharmonic behavior might be caused



FIGURE 3. Scanning electron microscopy images illustrating the superharmonic resonances in a ZnO nanowire that are not predicted by classical rod theory. (a)–(q) show the evolution of vibration amplitudes for increasing frequency number n.

by ordinary nonlinear driving at large amplitudes¹² or by the purely isotropic parametric resonance observed in previous studies.⁹

Theoretical Charge-Imbalance Resonance Model. We now investigate the material effects of ion beam exposure on a ZnO nanowire using theory as well as Molecular Dynamics (MD) simulations, in order to show how ion-beaminduced electric charge imbalance can produce the observed superharmonic resonances. As the projectile Ga⁺ ions from the FIB enter the ZnO surface and collide with a lattice atoms, they can create vacancies by ejecting lattice atoms from their position. After gradually losing energy due to electronic and nuclear collisions, the Ga⁺ ions eventually come to a stop and remain implanted within the ZnO lattice unless they had been backscattered away from the nanowire during the interaction.¹³ The SRIM software developed by Ziegler et al. was employed to simulate the implantation of Ga⁺ ions into a ZnO target with different ion beam energies.¹⁴ Using SRIM, we have estimated the depth of ion

TABLE 1.	The Superharmonic Resonant Frequencies Measured
in an FIB-E	xposed ZnO Nanowire and the Corresponding
Vibration A	Amplitudes

resonant frequency (kHz)	max amplitude (μ m)		
2.975	3.860		
3.168	4.210		
3.389	4.475		
3.640	4.739		
3.933	5.177		
4.275	5.791		
4.684	5.615		
5.182	7.195		
5.791	8.770		
6.564	9.125		
7.577	10.354		
8.960	12.284		
10.954	14.214		
14.082	15.272		
19.731	17.022		
32.782	20.092		
98.463	30.881		
198.893	>80		



FIGURE 4. A direct comparison of observed superharmonic frequencies and calculated values shows an excellent agreement between experiment and theory. The error line represents the percent difference between observed and predicted values.



FIGURE 5. Cross sections of the interaction volume of a Ga⁺ ions onto a ZnO target, for two values of beam energy \tilde{E} and incidence angle α , as calculated using the SRIM software: (a) $\tilde{E} = 10$ keV and $\alpha = 52^{\circ}$; (b) $\tilde{E} = 30$ keV and $\alpha = 52^{\circ}$; (c) $\tilde{E} = 10$ keV and $\alpha = 0^{\circ}$; (d) $\tilde{E} = 30$ keV and $\alpha = 0^{\circ}$.

implantation within a nanowire; the nature and proportion of lattice defects such as vacancy creations, interstitials, and substitutions; and the percentage of Ga⁺ ions that are backscattered from the ZnO surface. For this purpose, the SRIM simulations were performed by colliding 1000 successive Ga⁺ ions into a ZnO target. These simulations were performed both for ion beams entering the sample perpendicularly to the surface and at an incidence angle of 52° relative to the normal, which are the standard impact angles for the dual-beam FIB setups. In keeping with the experimental conditions described above for ion exposure, our numerical calculations assume a typical FIB apparatus with an ion beam energy E = 30 keV and a beam current of 100 pA.¹⁵

The implantation cross sections obtained in SRIM are shown in Figure 5. The implantation depth ranges from 80 to 280 Å, which corresponds to 2-7% of the thickness of the nanowire. The visual cross-section also shows that there is a sharp cutoff between the implanted region and the deeper volume where few Ga⁺ ions are implanted. There-

fore, contrary to what has been suggested by Weissenberger et al.,¹⁶ the effect of FIB implantation appears not to be distributed through the entire thickness of ZnO nanowires but rather limited to a superficial layer on the exposed face. The density of implanted Ga⁺ ions within the nanowire subsurface is then calculated by taking into account the nanowire's dimensions (200 nm \times 40 μ m), the fraction of the ion beam cross section which interacts with the nanowire (determined by the magnification level used), and the depth of the implantation layer (on the order of 100 Å). On the basis of the results obtained in SRIM and giving an exposure time of order t = 30 s, the density of implanted Ga⁺ ions and the density of final vacancies are found to be $\rho_{\rm ion} = 0.015$ ions per unit cell and $\rho_{\rm v} = 0.2$ vacancies per unit cell, respectively (see Table 2). Here we consider only the effect of final vacancies remaining in the lattice after exposure, since it has been shown that only ~ 1 % of vacancy creations remain in ZnO after FIB exposure due to strong dynamic annealing.⁴

We have modeled a ZnO nanowire structure using lattice properties obtained in SRIM simulation. Subsequent MD calculations of this replicated structure, performed using Materials Studio GULP and Forcite, indicate that the combined effect of lattice vacancies and implanted Ga⁺ ions leads to a reduction in elasticity of 40-50%. It is known that even with a slight change in the nature of atomic bonding, the elasticity of nanostructured material can vary significantly.¹⁷ According to the MD calculations, the numerical values for the elasticity modulus of untreated and FIBexposed ZnO are 426 and 182 GPa, respectively. The calculated value for the elasticity modulus of bulk ZnO is significantly larger than the accepted experimental value (140 GPa), but this is consistent with most other studies that have numerically estimated the elasticity of ZnO and other metal oxides.¹⁸ Indeed, there is currently a scientific consensus that MD simulations tend to overestimate the elasticity of ZnO compared to experimental values, and it has been

beam energy	backscattered ions (%)	vacancies per ion	implantation depth (Å)	lateral extent of penetration (Å)	$ ho_{ ext{ion}}$	$ ho_{ m v}$
10 keV (0°)	0.3	130	80	50	0.018	2.3
30 keV (0°)	0.0	390	140	50	0.010	4.0
10 keV (52°)	6.1	130	40	60	0.033	4.3
30 keV (52°)	5.6	390	90	110	0.015	5.8

TABLE 2. Implantation Properties of a ZnO Nanowire Exposed to an FIB with Beam Energies 10 and 30 keV and with Incidence Angles 0° and $52^{\circ^{a}}$

^{*a*} The proportion of backscattered ions, the number of vacancy events per incident Ga⁺ ion, and the implantation depth are calculated directly from calculations in SRIM. The resulting density of implanted Ga⁺ ions and of vacancy events (per unit cell), ρ_{ion} and ρ_{v} , respectively, are derived using the results from SRIM as well as the nanowire geometry.

suggested that these simulations may actually be more accurate than experimental results due to the presence of surface contaminants and oxide layers which decrease the observed elasticity of ZnO.¹⁹ Upon FIB exposure, the implanted surface also experiences a slight increase in mass density due to Ga⁺ ions which remain within the lattice. Assuming the ion density ρ_v calculated above within the implanted region and using the mass density of Ga (70 g/mol), it is found that the FIB implantation leads to an increase of 0.07 g/cm³. This represents a negligible increase of 1 % compared to the density of untreated ZnO (5.606 g/cm³). Thus, the elasticity of the nanowire is reduced in the region affected by ion implantation, while the mass density remains approximately unchanged. However, these mechanical changes alone cannot acount for the appearance of ultralow resonances in the FIB-exposed ZnO nanowires.

Although untreated ZnO acts a semiconductor, FIB exposure can also lead to important changes in the material's ability to conduct electric charge. Kucheyev et al. observed that FIB bombardment using light ions in the megaelectronvolt range increases the resistance of ZnO by as much as 7 orders of magnitude as charge carriers become "trapped" due to the effects of FIB implantation.²⁰ Additionally, Weissenberger et al. have reported an increase in electrical resistance in ZnO nanowires by a factor of 1000 for Ga^+ ion doses of approximately 10¹⁴ ions per cm^{2,16} Due to the implantation of positive Ga⁺ ions and the simultaneous escape of secondary electrons, FIB exposure can thus introduce an imbalance between the electric charge density of the ZnO nanowire's exposed and unexposed faces. One can obtain an estimate for the magnitude of this charge imbalance by assuming a static accumulation of positive electric charge on the FIB-exposed face and regular conducting behavior in the unexposed face. This yields an imbalance of approximately $\Delta q = 3 \times 10^8 \text{ C/m}^3$, although this estimate does not take into account the possibility of deeper Ga⁺ implantation into the unexposed section of the nanowire which can occur in case of ion tunneling. The effect of ion tunneling is negligible to first order due to the strongly annealing properties of ZnO.

We now derive a model that describes the ultralow superharmonic resonance of a ZnO nanowire due to charge imbalance. The diagram in Figure 6 schematically shows the effect of nonuniform charge distribution on the



FIGURE 6. Schematic diagram of a ZnO nanowire exposed to FIB on its left face. The accumulation of positive charge on the implanted side leads to charge imbalance, which in turns leads to a bending moment along the length of the nanowire. This bending moment leads to the appearance of FIB-induced superharmonic resonance.

balance of forces in a cross-sectional element of the nanowire. From the Lorentz force law, each infinitesimal section of the nanowire experiences a force due to the external electric field that is proportional to its own electric charge as well as to E(t), the oscillating external field, and points in the direction of E. Because the FIBexposed face of the nanowire contains more positive charge than the unexposed face, it experiences a stronger force from the oscillating field than the unexposed face does. When the deflection, θ , is nonzero, the axial component of this force on the FIB-exposed face is therefore larger than the corresponding axial component exerted on the unexposed face. The force imbalance gives rise to a moment (or torque) whose magnitude depends on the angle between the nanowire axis and the direction of the external electric field. Specifically, the magnitude of this force imbalance scales with $sin(\theta)$ because the axial forces on either face of the nanowire are both proportional to



FIGURE 7. The comparison of resonance amplitude behaviors for the case where $q \propto 1/\Omega^2$ (as predicted by FIB-induced superharmonic resonance), and the case where q = constant (such as for a driven pendulum). The *y*-axis represents Im(λ), which indicates the vibrational amplitude of the system under damped conditions. The graph shows that for q = constant, the resonance amplitude is almost zero for frequency numbers $n \leq 2$, while the resonance amplitudes remain large in the case where $q = q(\Omega)$ even well below the natural frequency. This implies that the observed resonances are indeed due to charge imbalance.

 $sin(\theta)$. Thus, the element at position *x* along the nanowire experiences an additional bending moment of the form

$$\Delta M(x, t) = M_0 \sin(\Theta) \Delta q \mathbf{E}(t)$$
(2)

where M_0 is a constant determined by the geometry of the nanowire and the mode shape, $\mathbf{E}(t) = \mathbf{E}_0 \cos \Omega t$ is the oscillating external electric field, Δq is the charge imbalance between the FIB-exposed and unexposed side of the nanowire, and Θ is the angle between the nanowire axis and the direction of **E**. Denoting the lateral displacement at position *x* along the nanowire as U(x), the sin(Θ) term can be expanded as

$$\sin(\Theta) = \frac{U}{\sqrt{U^2 + x^2}} \approx \frac{U}{x}$$
(3)

The vibrational equation of motion (EOM) of a nanowire containing charge imbalance driven by an external electric field is therefore:

$$YI\frac{\partial^4 U(x,t)}{\partial x^4} - \frac{8\zeta_0}{L^3}\cos(\Omega t)U(x,t) + \rho A\frac{\partial^2 U(x,t)}{\partial t^2} = f(x,t)$$
(4)

where $\zeta_0 = M_0 \Delta q E_0$ and we have kept only the dominant term in the expansion of (U/x)'' and eliminated the *x*-

dependence of the problem by averaging x^3 over the length of the nanowire, denoted *L*. This equation is identical to the EOM of a classical Euler beam, with the addition of a parametric term which depends on both the dependent variable *t* and the independent variable *U*. Because the effect of the external driving force, f(x,t), is already well-understood, we consider the homogeneous problem in which the only forcing term comes from the parametric term $8\zeta_0/L^3$ $\cos(\Omega t)U(x,t)$. A damping term proportional to $\partial U/\partial t$ is sometimes included in the equation of motion, but it has been shown that this damping has little effect on the value of the resonance frequencies due to a high *Q* factor between 10 and 100.²¹ Therefore, this term is also omitted here for mathematical simplicity.

Since the effect of charge imbalance is small compared with the driving force at the tip, we may use a perturbation approach in which the mode shapes, X(x), are still related to the wavenumber *k* by the relation $X^{(4)}(x) = k^4 X(x)$, as in the classical case. After separating variables and defining some new parameters, the EOM can be directly rewritten as a Mathieu equation

$$\frac{\partial^2 u}{\partial \tau^2} = -(a - 2q\cos 2\tau)u \tag{5}$$

where $a = (2\omega_0/\Omega)^2$, $q = 16\zeta_0/(\rho AL^3\Omega^2)$, and $\tau = \Omega t/2$. The Mathieu equation is most commonly known for governing the response of a classical pendulum with a vertically driven support. A crucial result from parametric oscillation theory is that there exists a discrete set of driving frequencies Ω

for which the solution is resonant.²² Each resonant frequency range has a finite width, determined by the magnitude of the charge imbalance Δq , and is centered at the superharmonic resonance frequency

$$\omega_n = \frac{2\omega_0}{n} \tag{6}$$

where ω_0 is the natural resonance frequency. Thus, the appearance of charge imbalance from FIB in a ZnO nanowire theoretically leads to parametric vibration and its associated superharmonic resonances.

In our experiment, the ion-beam exposure mechanism has led to superharmonic resonances up to a high order (as high as n = 132). The experimental results described above provide a method for verifying that the amplitudes of chargeimbalance-induced parametric resonance follow the behavior predicted by eq 5. In order to compare the observed resonance amplitudes with the amplitude behavior predicted by the charge-imbalance resonance model, we note that the parameter q in eq 5 is proportional to $1/\Omega^2$. This is because the magnitude of the parametric forcing increases with the magnitude of the restoring force in the case of FIB-induced parametric resonance. In contrast, the parameter q is typically independent of Ω in most occurrences of the Mathieu equation (e.g., in the canonical case of a driven pendulum).²³ Whether or not q depends on Ω has a significant influence on the evolution of the amplitude associated with each superharmonic resonance frequency ω_n . The amplitude dependence has been plotted as a function of the driving frequency Ω in the case predicted by charge imbalance (that is, when q is proportional to $1/\Omega^2$) as well as the case where q is independent of Ω in Figure 7. The amplitude is expressed in terms of the rate of divergence of the undamped system, which is given by the imaginary part of the characteristic exponent associated with the EOM (as obtained from Floquet theory for parametric vibrations).²³ The resonance peaks occur at the same frequencies in both cases, but for q= constant, the peak immediately below ω_0 has dropped to 0.01 and the subsequent peaks have practically zero height. In contrast, the peaks corresponding to charge imbalance decay slowly for resonance frequencies below ω_0 , meaning that significant resonance should still occur as low as $\omega_0/15$ or even $\omega_0/66$ (not shown in the figure). Since the experimentally observed resonance amplitudes also decay slowly with frequency number n, it follows that these observed amplitudes point to charge imbalance as a cause of the superharmonic resonances as opposed to an alternative mechanism of the driven-pendulum type. The theoretically derived evolution of resonance amplitude for increasing parametric order n demonstrates the unique properties of the charge-imbalance mechanism, which enables the appearance of parametric resonance at higher order than previously possible.

Conclusion. We have investigated a mechanical phenomenon that is unprecedented in the field of elastic rod vibration. While the resonance behavior of regular nanowires is dictated by classical elasticity theory, we have shown that partial ion-beam exposure can lead to high-order parametric resonance due to charge imbalance. From the perspective of future applications, these results are promising because they suggest the application of ion implantation as a reliable technique for tuning the resonance of nanodevices. By enabling resonance to occur at frequencies two orders below the natural frequency, this method opens a new range of applications for vibrating functional nanowires. In fine-tuning the level of exposure to an ion beam, we should be able to further lower the superharmonic resonance frequency of nanowires to increase their resonance sensitivity for ultraprecise sensors, energy-scavenging devices, and other nanodevices.

Acknowledgment. The authors thank Kirk McDonald, Joshua Shaevitz, and Nai-Phuan Ong for useful discussions. This work is supported in part by the National Science Foundation-MRSEC program through the Princeton Center for Complex Materials (DMR-0819860).

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