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Toward Robust Nanogenerator Using Aluminum Substrate

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Introduction

As the energy crisis and global warming are emerging as major issues, the development of renewable and green energy based on alternative energy resources such as solar, wind, hydrogen or geothermal sources, has attracted considerable interest.[1–5] The energy harvesting technologies based on these natural resources have been well established, and their use has gradually increased. Yet there are still many forms of energy sources in our living environment, which are not being utilized. Mechanical energy is one of the most representative sources that can be artificially generated from vibration, human walking, movement of automobiles, etc., which are abundant in the living environment, but all of which are usually wasted. In recent years, we have developed the nanogenerators (NG) that harvest this abandoned mechanical energy with variable frequencies and amplitudes via the piezoelectric effect.[6–14] The fundamental mechanism of a NG is related to a piezoelectric potential generated in nanowires (NWs) when they are dynamically strained under an external force, and the corresponding transient current that flows to balance the Fermi levels at two contacts. Further improvement in their performance has been achieved by pretreatment of ZnO NW arrays, which could drive an electrical watch for a few minute after an accumulation of the resulting charge.[15] Despite its advantages, the NG is still difficult to apply to energy harvesting device to scavenge the mechanical energy from the environment owing to high cost, low-throughput process, and weak durability. Thus, it is critically necessary to develop innovative strategies toward achieving cost-effective, large-area and robust NG in order to consistently harvest the mechanical energy from the environmental sources for an extended period.

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In this work, we report a robust and large-area NG-based on cost-effective Al electrodes which could enable energy harvest from the walking motions. ZnO NW arrays were uniformly grown on a large-area Al foil surface with the size of 5 cm × 6 cm, which was also used as an electrode. In order to prevent the detachment of ZnO NWs from the substrate at the boundary interface under an applied strain, a micro-scale rough surface of the Al foil was produced to increase the surface contact area by sandblasting prior to the growth of ZnO NW. Multiple NGs were easily integrated in parallel and serial connections for increasing the output voltage and current. The maximum output voltage from the three-layer stacked NG with serial connections reached 0.43 V, and the maximum output current density from the parallel integration with three units of them approached the 54 nA/cm^2. Furthermore, three-dimensionally integrated NG, which was respectively composed of three units in width, length, and height, demonstrated the potential to work as an energy harvesting device under the human walking; the maximum output voltage exceeded 3 V and the maximum output current reached 195 nA. This is a key step towards a development of robust energy harvesting devices for practical use in an environment where dynamic stress/strain is available, such as the road where people can not only walk but also drive their cars.

In general, since a cost-effective and lightweight Al is not only an excellent electrical conductor but also a recyclable material without downgrading of its qualities, it has been extensively used in various industries. So instead of Au-coated substrates which have been used as an electrode for NG,[10,11,13–15] we used an industrial Al foil of 99.5% purity with the thickness of 0.1 mm as electrodes as well as substrate. Once ZnO NWs are grown on the one side of Al foil only, the other side can be used as upper electrode of lower unit, as shown in **Figure 1**a. Furthermore, ZnO NWs are uniformly grown on the large-area sandblasted Al surface because of their hydrophilicity. In the chemical growth process of ZnO NWs, the NWs are grown on the sputter-coated seed layer surface by placing the substrate at the top of the nutrient solution with the face down at 85 °C.[16,17] During this process, bubbles generated in the solution rise to the solution surface and are often trapped at the face-down substrate surface, preventing uniform growth of ZnO NWs on the large-area surface. However, the sandblasted Al surface exhibits enhanced hydrophilicity due to the increased roughness as well as the surface oxidation during the sandblasting process.[18] Consequently, the bubbles do not adhere to the surface as the molecules of the solution are strongly attached to the hydrophilic surface.[19] For this reason, ZnO NWs grow uniformly on the large-area Al surface. As a result, three-dimensional integrated NG in parallel and series can be easily designed for increasing the output voltage and current (See Figure 1a and Figure S1 in

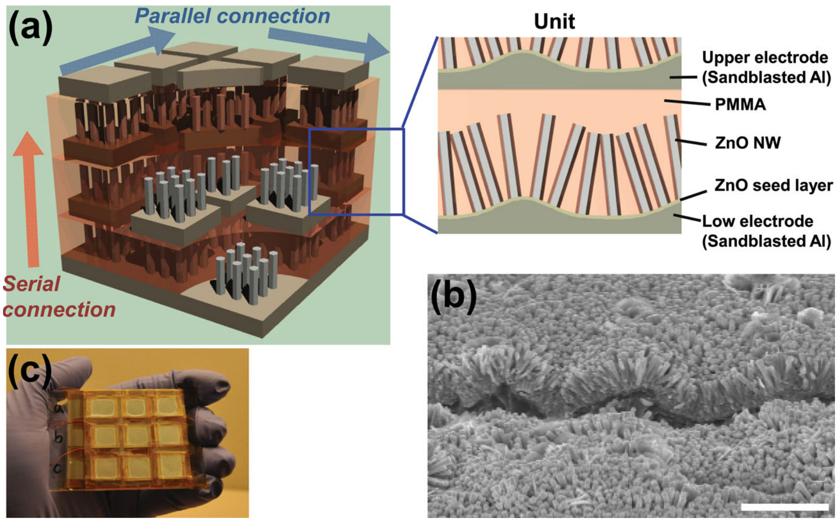

Figure 1. Parallel and serial integrated NG device based on Al substrate. (a) Scheme of NG integrated in parallel and serial for enhancing output current and voltage. The NG unit in device simultaneously used Al substrate as upper and lower electrodes. (b) SEM image of as-grown ZnO NWs on sandblasted Al substrate with micro-roughness. Scale bar: 5 μm (c) Photographic image of the NG device integrated in parallel and serial.

Supporting Information). The densely grown ZnO NWs on the sandblasted Al surface with micro-roughness was confirmed from a field-emission scanning electron microscope (FE-SEM) image (Figure 1b). Figure 1c shows an optical image of the NG with 27 unit cells in series and parallel with the overall size of 5×6 cm^2.

In the chemical growth process, the ZnO NWs with uniform size are well grown on the substrate with a seed layer, such as ZnO and Au. However, when these samples were under the external force such as bending, the ZnO may be easily detached from the substrate possibly due to the strain differences at the boundary interface between the brittle ZnO and the flexible substrate. In the previous results, to enhance the mechanical durability and flexibility, polymers have been used for coating ZnO NWs and packaging the device.[13–17] On the other hand, the ZnO NWs grown on the sandblasted Al foil with micro-roughness have an excellent durability owing to the increased surface contact area between ZnO seed layer and Al substrate. To demonstrate their durability, we prepared the samples with the bending radius of 3 mm by rolling up it with a ballpoint pen lead, as shown in **Figure 2**a. Figure 2b shows its SEM image, and Figure 2c and 2d show the magnified SEM images in circular and rectangular dotted line in Figure 2b, respectively. Although some cracks marked with arrows in Figure 2c were found, there was no region that was peeled off the Al substrate. Furthermore, ZnO NWs were attached securely on the substrate near the edge cut with a scissor, as shown in Figure 2d. This is probably due to the increased surface contact area that leads to a firm bonding between the two surfaces. Moreover, the increased outer surface area may also reduce the surface strain of Al substrate when the substrate is bent. Therefore, it could eventually reduce the strain difference at the interface between the ZnO and the substrate. On the other hand, in the case of ZnO NWs grown on flat Al, ZnO layer was easily detached from the substrate surface under the identical conditions (See Figure S2 in Supporting Information). In particular, the large layers of ZnO peeled off the substrate provide evidence that the detachment could be caused by the strain differences at the boundary interface between the brittle ZnO and the flexible Al substrate. Thus, ZnO NWs grown on the surface with micro-roughness exhibits an excellent durability under an external force.

The working principle of the NG is related to the coupling of piezoelectric and semiconducting properties. When a stress is applied by an external force, the ZnO NWs grown parallel to the c-axis are under uniaxial compression. A negative and positive piezoelectric potential are respectively occurred at the top and bottom side of ZnO NWs, the corresponding transient current flows from the tip to the bottom through the external circuit, which is detected as an electric pulse. As the compressive strain is released by removal of the external force, the piezoelectric potential in the NWs is disappeared. As a result, the electrons flow back via the external circuit, creating an electric pulse in the opposite direction. These electric pulses can be accumulated, and the amount can be significantly enhanced by integration in parallel and series.

The NG based on an Al substrate can be easily integrated in series and parallel for increasing the output voltage and current

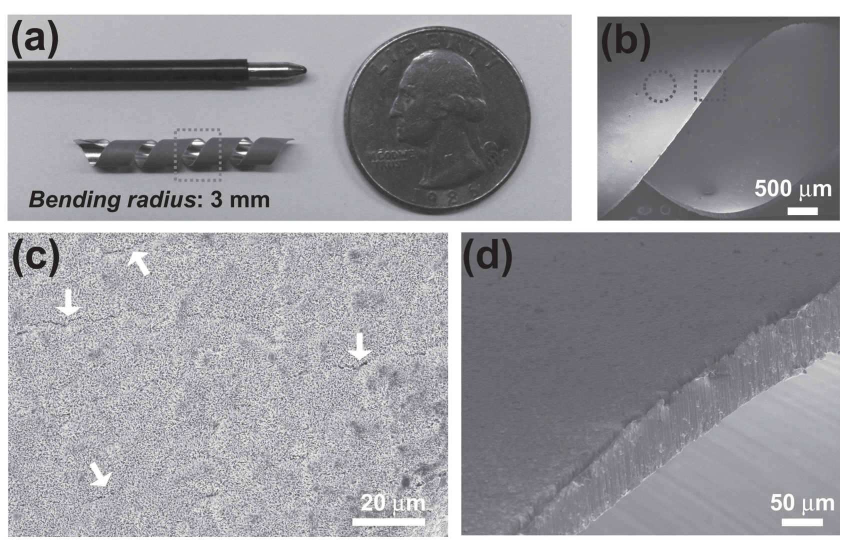

Figure 2. Durability of ZnO NWs on sandblasted Al substrate. (a) Photographic and (b) SEM image of the ZnO NWs-grown Al substrate with the bending radius of 3 mm by rolling up it with a ballpoint pen lead. Magnified SEM images in (c) rectangular and (d) circular dotted line in (b).

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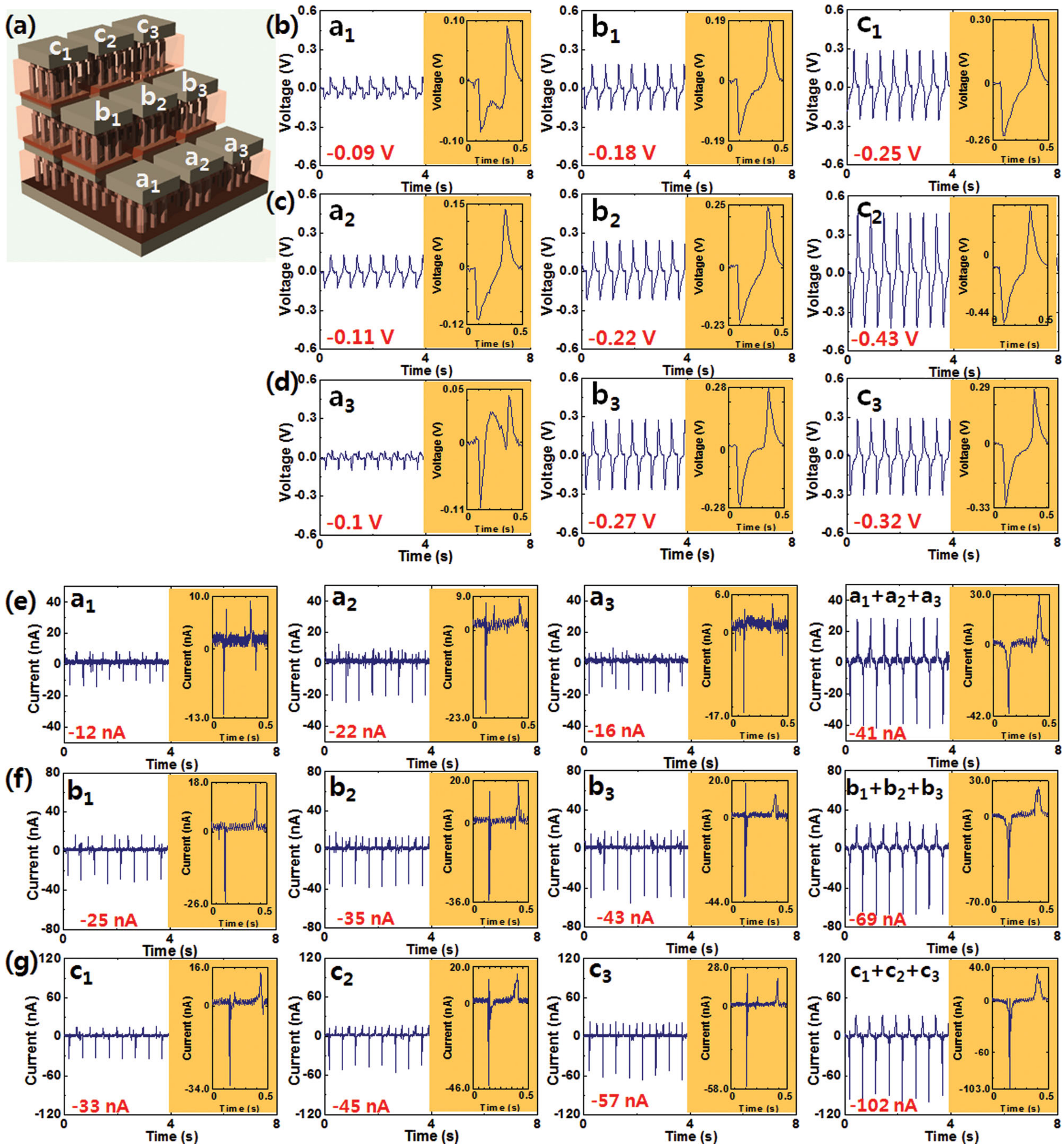

Figure 3. Output voltage and current of NG device integrated in parallel and serial. (a) Scheme of the integrated NG to demonstrate the possibility of scale-up for enhancing the output voltage and current. Output voltage depending on the increase of the number of serially integrated unit; (b) one unit, (c) two units, and (d) three units. Output current of NG integrated in parallel with three parts connected in series with (e) one unit, (f) two units, and (g) three units.

owing to the uniform growth of ZnO NWs on large-area substrate and the simultaneous use of the Al substrate as lower and upper electrodes. To demonstrate the possibility of scale-up, we designed NG device integrated in series and parallel to characterize the electrical performance of the device, consisting of nine parts on the large-area Al electrode, as shown in **Figure 3**a; the first line, including a_1, a_2, and a_3, was integrated in parallel with three parts forming one unit; the second line, including b_1, b_2, and b_3, was integrated in parallel with three parts connected in series with two units; the third line, including c_1, c_2, and c_3, was integrated in parallel with three parts serially integrated with three units. To characterize the performance of each part of the NG device, the NG array was tested by a controllable trigger setup, which could periodically press and release at frequency of 2 Hz. To guarantee the measurement for each NG part is under same condition, the trigger in contact with the NG is standardized with the same materials and contact area of 9-mm diameter for each NG part. In case of a serial integration, we measured the output voltage under the same condition with the increase in the number of serially integrated unit. As the number of integrated units increase from 1 to 3 in the order of a_1, b_1, and c_1, their output voltages increase from 0.09, 0.18, and to 0.25 V, respectively, as shown in Figure 3b. Since the units integrated in series are simultaneously affected by same external force and their corresponding piezoelectric potential in external load is summed, the output voltage increases with the number of units. Likewise, the other serial integration came up with similar results, and these results clearly show the possibility of serial integration based on Al substrate, as shown in Figure 3c and 3d.

Then, when we measured the output current for the device integrated in parallel with three parts, the applied force was almost tripled compared of the force in the experiment for one part in order to supply the same level of strain to the device. Three parts, including a_1, a_2, and a_3, showed the output currents of 12, 22, and 16 nA and their parallel integration led to an output current of 41 nA, as shown in Figure 3e. Likewise, the other integration, which was composed of two- or three-layered NGs with the increased output current because of the enhancement of piezoelectric potential, led to an output current of 69 nA and 102 nA respectively, as shown in Figure 3f and 3g. Although the measured output of the parallel integrated NG was slightly less than the sum of the individual output, these results show not only the possibility of the parallel integration on the large-area substrate to increase the output current but also the evidence of uniform growth of ZnO NWs on the large-area substrate. In other words, the NG based on the Al substrate can be easily integrated not only in series for high output voltage but also in parallel for the high output current without size limit. To investigate their stability over an extended period, we continuously measured their output voltage for 20 hours at a frequency of 2 Hz using the serially integrated NG (C_2 part). The NG showed good stability after 20 hours of operation. (See Figure S3 in Supporting Information) Also, the output voltage was not significantly affected by an increase in the driving frequency from 2 to 8 Hz. (See Figure S4 in Supporting Information) Since the human walking and movement of automobiles are usually occurred at various low-frequencies, these stable results are promising for the use in the practical applications.

Since our device was aimed towards robust NG capable of harvesting energy from human walking, we designed three-dimensional integrated NG composed of three units in width, length, and height, as shown in **Figure 4**a. To prevent unexpected effect during operation which may cause undesired electrical noise, the device was firmly fixed on the flat supporting plate with the size of 29 × 13 cm^2. The interface between the device and the supporting plate was insulated by kapton tape with a thickness of ~15 μm. Under the human walking condition, the device exhibited maximum output voltage and current of about 3.2 V and 195 nA, respectively. (See Figure 4b–d and Video in the Supporting Information) Although the output varied depending on the force acting on the device was

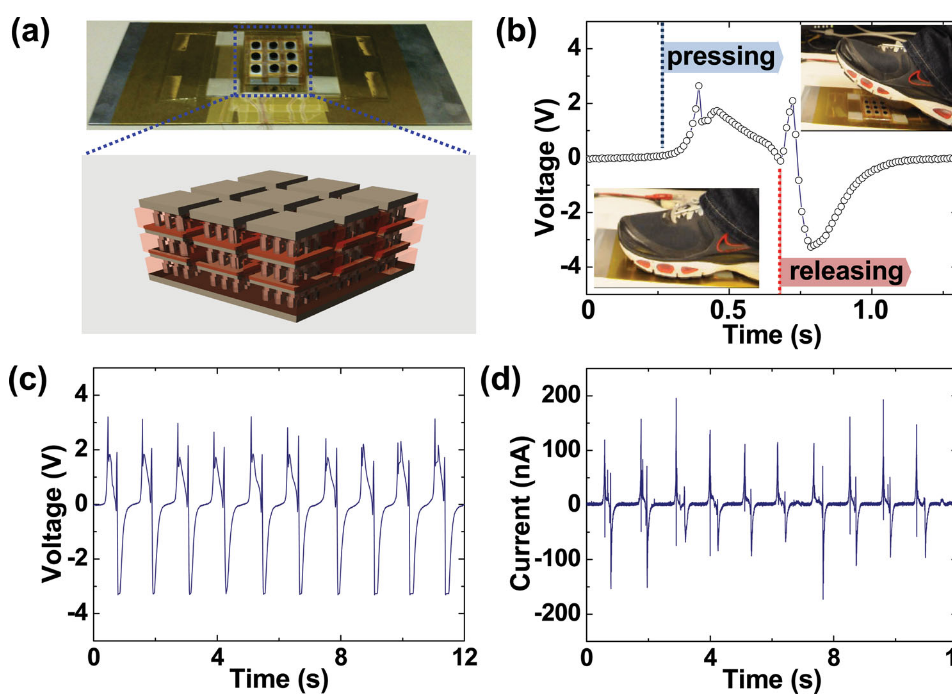

Figure 4. Performance depending on human walking. (a) Photograph image and scheme of three-dimensional integrated NG device. (b) Output voltage depending on the pressing and releasing during walking. An output voltage appeared on the event of the pressing and releasing action of the foot. (c) Output voltage and (d) output current of the device during walking.

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different, this result indicates that our device can produce the corresponding output power regardless of walking styles with different magnitudes and frequencies. In addition, our device can not only be integrated in parallel and series for high output without size and number limit but also be applied to the surface of various geometry/shape where the mechanical energy can be generated by the any kind of motion or vibrations owing to their robustness. These merits provide great potential in the field of renewable energy harvesting in addition to the present solar cells, fuel cells, aerogenerator and thermoelectric technologies.

In summary, we have successfully fabricated a robust and large-area nanogenerators based on cost-effective Al substrate. Employing micro-roughness surface produced by sandblasting, not only the large-area NG fabrication due to the enhanced hydrophilicity, but also the NG with higher mechanical durability due to the increased surface contact area between the ZnO and the substrate were achieved. Since the Al substrate in NG can be simultaneously used as upper and lower electrodes, simplified integration of NGs in parallel and/or series for enhancement of output current and voltage without size and number limit was demonstrated. Furthermore, three-dimensional integrated NG showed that the maximum output voltage and current reached up to 3.2 V and 195 nA, respectively, under the human walking condition. Our strategy can provide a highly promising platform as an energy harvester that convert mechanical motion of humans and automobiles into electricity.

Experimental Section

For the fabrication of nanogenerator, first, sand particles with the diameter of about 50 µm were ejected from a nozzle using compressed air to produce micro-roughness on the Al surface. The pressure of the compressed air is 4 kgf/cm^2, and the sandblasted Al substrates were rinsed with deionized water. And a 100-nm thick ZnO seed layer was deposited on the Al surface with micro-roughness by sputtering. Afterward, hydrothermal process was performed for the growth of ZnO NW arrays. The nutrient solution we used in this process was an equal molar aqueous solution of hexamethylenetetramine (HMTA) and zinc nitrate hexahydrate (ZnNO3 · 6(H2O)), resulting in a concentration of 0.1 M. During the process, the Al substrate was placed on the top of the solution with the face down. The growth process was carried out in a mechanical convection oven (model Yamato DKN400, Santa Clara, CA) at 85 °C for 16 h. The NW-grown Al substrates were rinsed with DI water and dried in air. The dimension of as-grown ZnO NW was about between 100 and 200 nm in diameter and 2 µm in length. For improving the output performance of the NG device, the ZnO NW-grown substrate was immersed into poly (diallydimethylammonium chloride) (PDADMAC) solution and poly (sodium 4-styrenesulfonate) (PSS) for 90, respectively.[15] Three NW-grown Al substrates with the size of 5 cm × 6 cm were prepared. One of them was used as the bottom electrode of the device to which one lead was connected. A 2-µm thick poly(methyl methacrylate) (PMMA) layer was spin-coated on the ZnO NW-grown surface of this substrate. The others were used as middle and top layer of the device for the integration in parallel and series. 2-µm thick PMMA layers were sequentially spin-coated on the top and bottom sides of the substrates. After drying in air, the substrates were cut into 9 units with the size of 1.1 cm × 1.4 cm. Each unit was stacked on the bottom layer and their edges were fixed by kapton tape. After stacking three layers, Al plates with the size of 1.1 cm × 1.4 cm were used as the topmost electrode and nine leads were connected to them, respectively. The output signal of the NG was recorded by using a low-noise voltage preamplifier (Standard Research System Model SR560) and a low-noise voltage current preamplifier (Standard Research System Model SR570). A sine servo controller (Labworks Ins. SC-121) and a linear power amplifier (Labworks Ins. PA-119) served to periodically pressing and releasing the NGs at a desired frequency and power.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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