# Chapter 1 Introduction of Piezotronics and Piezo-Phototronics

Abstract Starting from the road map for microelectronics, the focus of future electronics will be on functionalities toward personal, portable, polymer, sensor, and self-powering applications. The integration of these characteristics with the fast speed and high density as defined by Moore's law will lead to the development of smart systems and self-powered systems. This chapter first introduces the basic physics of piezotronics and piezo-phototronics from band structure theory. Then blue-prints for future impacts and applications of piezotronics and piezo-phototronics are presented. The role anticipated to be played by piezotronics in the era of "Beyond Moore" is similar to the mechanosensation in physiology that provides a direct human "interfacing" with CMOS technology. It presents a paradigm shift for developing revolutionary technologies for force/pressure triggered/controlled electronic devices, sensors, MEMS, human–computer interfacing, nanorobotics, touch-pad, solar cell, photon detector and light-emitting diodes.

## 1.1 Beyond Moore's Law with Diversity and Multifunctionality

Moore's law has been the roadmap that directs and drives the information technology in the last few decades. With the density of devices on a single silicon chip doubles every 18 months, increasing CPU speed and building a system on a chip are the major developing directions for IT technology. With the line width reaching close to 10 nm, a general question is how small a device can we fabricate at industrial scale? What are the pros and cons with respect to stability and liability when devices get extraordinarily small? Is the speed the only driving parameter that we should look for? We know that Moore's law will reach its limit one day, and it is just a matter of time. Then, the question is: what should we look for beyond Moore's law?

Sensor network and personal health care have been predicted as the major driving force for the near term industry. As we have observed in today's electronic products, electronics is moving toward personal electronics, portable electronics and polymer-based flexible electronics. We are looking for multifunctionality and diversity associated with electronics. Take a cell phone as an example, having a super fast computer in a cell phone may not be the major drive for future markets, but the consumers are looking for more functionality, such as health care sensors for blood



**Fig. 1.1** Future perspective of electronics beyond Moore's law. The *vertical axis* represents a miniaturization and increase of device density, CPU speed and memory. The *horizontal axis* represents the diversity and functionality for personal and portable electronics. The future of electronics is an integration of CPU speed and functionality. It is anticipated that an integration of mechanical action through piezotronics in electronic systems is an important aspect of interfacing human and CMOS technologies

pressure, body temperature and blood sugar level, interfacing with environment with sensors for detecting gases, UV, and hazardous chemicals. In such a case, the IT technology is developing along another dimension, as presented in Fig. 1.1. A conjunction of speed and functionality will be the future trend of electronics. The near future development of electronics is moving toward personal, portable and (flexible or organic) polymer-based electronics with the integration of multifunctional sensors and self-powering technology. The goal is to directly interfacing with human and the environment in which we live in. A combination of CPU speed, density of memory and logic with the functionality tends to drive the electronics toward smart systems and self-powered systems, which are believed to be the major roadmaps for electronics.

#### 1.2 Interfacing Human with Machine

Once we interface human with electronics, we are inevitably have to consider human activities and the "signals" generated by a human, which are mostly mechanical actions and a small portion of electrical signals. Electric signals transmitted by neuron system have been studied for decades and various approaches have been developed to interface neuron signals with silicon-based technologies using field effect transistors. Mechanical actions, however, is not easy to directly interface with silicon technologies without innovative design and approaches. The most conventional approach is to use sensors that are sensitive to strain variation. The signals from sensors can be detected and recorded by conventional electronics, which is so called passive detection, but they are unable to be used to control Si electronics. The current on-going research in flexible electronics is to minimize and eliminate the effect of strain introduced by the substrate on the performance of the electronic components built on a substrate, which can be termed the passive flexible electronics. On the other hand, we can utilize the deformation introduced by the substrate to induce electrical signals that can be used directly for controlling Si-based electronics. A "mediator" or "translator" is needed for conjunction of biomechanical action with the operation of silicon-based electronics. Piezotronics and piezo-phototronics were invented for such purposes, and they are considered as the *active* flexible electronics or bio-driven electronics. This is an approach for directly generating digital signals and control using mechanical actions.

The role anticipated to be played by piezotronics is similar to the mechanosensation in physiology [1]. Mechanosensation is a response mechanism to mechanical stimuli. The physiological foundation for the senses of touch, hearing and balance, and pain is the conversion of mechanical stimuli into neuronal signals; the former is mechanical actuation and the latter is electrical stimulation. Mechanoreceptors of the skin are responsible for touch. Tiny cells in the inner ear are responsible for hearing and balance.

## **1.3 Piezopotential—The Fundamental Physics for Piezotronics** and Piezo-Phototronics

Piezoelectricity, a phenomenon known for centuries, is an effect that is about the production of electrical potential in a substance as the pressure on it changes. The most well-known material that has piezoelectric effect is the provskite structured  $Pb(Zr, Ti)O_3$  (PZT), which has found huge applications in electromechanical sensors, actuators, and energy generators. But PZT is an electric insulator and it is less useful for building electronic devices. Piezoelectricity has its own field and is being largely studied in the ceramic community. Wurtzite structures, such as ZnO, GaN, InN, and ZnS, also have piezoelectric properties but they are not extensively used as much as PZT in piezoelectric sensors and actuators due to their small piezoelectric coefficient. Therefore, the study of wurtzite structures is mainly in the electronic and photonic community due their semiconductor and photon excitation properties.

Silicon-based CMOS technology is operated by electrical driven charge transport process. To directly control the operation of CMOS by mechanical action, one must find an electric signal that can be generated as a result of mechanical action. The most nature choice is piezoelectricity. As for this purpose, we choose the Wurtzite





materials, such as ZnO, GaN, InN, and ZnS, which simultaneously have piezoelectric and semiconductor properties. ZnO, for example, has a non-central symmetric crystal structure, which naturally produces piezoelectric effect once the material is strained. Wurtzite crystal has a hexagonal structure with a large anisotropic property in *c*-axis direction and perpendicular to the *c*-axis. Simply, the Zn<sup>2+</sup> cations and O<sup>2-</sup> anions are tetrahedrally coordinated and the centers of the positive ions and negatives ions overlap with each other. If a stress is applied at an apex of the tetrahedron, the center of the cations and the center of anions are relatively displaced, resulting in a dipole moment (Fig. 1.2(a)). A constructive add-up occurs of the dipole moments created by all of the units in the crystal results in a macroscopic potential drop along the straining direction in the crystal. This is the piezoelectric potential (*piezopotential*) (Fig. 1.2(b)) [2]. Piezopotential can serve as the driving force for the flow of electrons in the external load once subject to mechanical deformation, which is the fundamental of the nanogenerator [3–6].

The distribution of piezopotential in a *c*-axis ZnO nanowire (NW) has been calculated using the Lippman theory [7–9] without considering the doping in ZnO. For a NW with a length of 1200 nm and a hexagonal side length of 100 nm, a tensile force of 85 nN creates a potential drop of approximately 0.4 V between the two ends, with the +c side positive (Fig. 1.2(b)). When the applied force changes to a compressive strain, the piezoelectric potential reverses with the potential difference



**Fig. 1.3** Piezopotential created inside a nanostructure, as represented by the color code, is the fundamental physics for nanogenerator and piezotronics. (a) Nanogenerator is based on a process of piezopotential driven flow of electrons in the external load. (b) Piezotronics is about the devices fabricated using a process of piezopotential tuned/controlled charge carrier transport at the metal–semiconductor interface or p–n junction. Piezo-phototronics is about the devices fabricated using piezopotential to control charge carrier generation, separation, transport and recombination processes at the interface/junction

remaining 0.4 V but with the -c-axis side at a higher potential. The creation of this inner crystal potential is the core of piezotronics.

The presence of the piezopotential in the crystal has created a few new research fields. A nanogenerator has been developed for converting mechanical energy into electricity [10–13]. Once a strained piezoelectric crystal is connected at its two polar ends to an external electric load, the piezopotential creates a drop in the Fermi levels at the two contact ends, thus, the free electrons in the external load are driven to flow from one side to the other to "screen" the local piezopotential and reach a new equilibrium. The generated current in the load is a result of the transient flow of electrons. An alternating flow of electrons is possible if the piezopotential is continuously changed by applying a dynamic stress across the crystal. This means that the nanogenerator gives continuous output power if the applied stress is varying, which means inputting mechanical work (Fig. 1.3(a)). The nanogenerator has been extensively developed and it is now gives an output of  $\sim$ 3 V, and the output power is capable to drive a liquid crystal display (LCD), light-emitting diode and laser diode [14–17]. The nanogenerator will play an important role in energy harvesting as the sustainable and self-sufficient power source for micro/nanosystems.

#### **1.4 Coining the Field of Piezotronics**

In 2006, two independent research experiments were carried out in Wang's group. The first group of experiment was to measure the electric transport of a long ZnO wire, the two ends of which were completely enclosed by electrodes, as its shape being bent inside a scanning electron microscopy (SEM) [18]. A dramatic drop in electric conductance was obtained as the degree of bending increased. The interpretation was that a piezoelectric potential drop was created across the wire when it is bent, which acted as a gate voltage for controlling the transport of charge carriers through the wire. This is referred to piezoelectric field effect transistor (PE-FET).

The second experiment was about a two-probe manipulation of a single ZnO NW and measurement of its transport property [19]. One probe held one end of a nanowire (NW) that laid on an insulator substrate, the other probe pushed the NW from the other end by in-contact with the tensile surface of the NW. The tungsten tips had Ohmic contact with the NW. The I-V curve changed from a linear shape to a rectifying behavior with the increase of the degree of NW bending. This phenomenon was interpreted as a result of creating a positive piezopotential at the interface region, which served as potential barrier for blocking the flow of electrons to one direction. This is the piezoelectric-diode (PE-diode).

Both the PE-FET and PE-diode were based on the presence of a strain induced piezoelectric potential in the NW. The induced flow of electrons in the external circuit by the piezoelectric potential is the energy generation process. The presence of the piezopotential can drastically change the transport characteristic of a NW-based FET. To systematically represent the piezoelectric-semiconductor coupled properties of such a system, Wang introduced the concept of nano-piezotronics on Nov. 24, 2006 and publicly disclosed it in the MRS fall conference in Boston a few days later [20]. Then, Wang first coined the word of piezotronics in a short paper published in 2007 [21, 22]. The basis of piezotronics is to use piezopotential to tune and control the transport of the carriers inside the nanowire (Fig. 1.3(b)). Ever since then, dramatic progress has been made in piezotronics, which will be described in the following chapters.

#### **1.5 Piezotronic Effect**

A most simple FET is a two ends bonded semiconductor wire, in which the two electric contacts at the ends are the source and drain, and the gate voltage can be applied either at the top of the wire through a gate electrode or at its bottom on the substrate. By applying a source to drain driving voltage,  $V_{\rm ds}$ , the charge carrier transport process in the semiconductor device is tuned/gated by the gate voltage  $V_{\rm g}$ , which is an externally applied potential.

Alternatively, the gate voltage can be replaced by the piezopotential generated inside the crystal (inner potential), so that the charge carrier transport process in FET can be tuned/gated by applying a stress to the device [20]. This type of devices is called piezotronic devices as triggered or driven by a mechanical deformation action. When a ZnO NW is strained axially along its length, two typical effects are observed. One is the *piezoresistance effect*, which is introduced because of the change in bandgap and possibly density of states in the conduction band. This effect

has no polarity so that it has equivalent/identical effect on the source and drain of the FET. On the other hand, piezopotential is created along its length. For an axial strained NW, the piezoelectric potential continuously drops from one side of the NW to the other, which means that the electron energy continuously increases from the one side to the other. Meanwhile, the Fermi level will be flat all over the NW when equilibrium is achieved, since there is no external electrical field. As a result, the effective barrier height and/or width of the electron energy barrier between ZnO and metal electrode will be raised at one side and lowered at the other side, thus, it has a non-symmetric effect on the barrier heights at the source and drain. Therefore, *piezotronic effect* is to use piezopotential to tune/control the charge transport across an interface/junction [22, 23].

#### 1.5.1 Piezotronic Effect on Metal–Semiconductor Contact

A better understanding about the piezotronic effect is to compare it with the most fundamental structure in semiconductor devices: Schottky contact and p–n junction. When a metal and a n-type semiconductor forms a contact, a Schottky barrier (SB)  $(e\phi_{SB})$  is created at the interface if the work function of the metal is appreciably larger than the electron affinity of the semiconductor (Fig. 1.4(a)). Current can only pass through this barrier if the applied external voltage is larger than a threshold value  $(\phi_i)$  and its polarity is with the metal side positive (for n-type semiconductor). If a photon excitation is introduced, the newly generated electron–hole pairs not only largely increase the local conductance, but also the effective height of the SB is reduced as a result of charge redistribution at the interface (Fig. 1.4(b)).

Once a strain is created in the semiconductor that also has piezoelectric property, a negative piezopotential at the semiconductor side effectively increases the local SB height to  $e\phi'$  (Fig. 1.4(c)), while a positive piezopotential reduces the barrier height. The polarity of the piezopotential is dictated by the direction of the *c*-axis for ZnO. The role played by the piezopotential is to effectively change the local contact characteristics through an internal field, thus, the charge carrier transport process is tuned/gated at the metal–semiconductor (M–S) contact.

Strain in the structure would produce piezo-charges at the interfacial region. It is important to note that the polarization charges are distributed within a small depth from the surface and they are ionic charges, which are non-mobile charges located adjacent to the interface. In such a case, free carriers can only partially screen the piezo-charges due to the finite dielectric permittivity of the crystal and the limited doping concentration, but they cannot completely cancel the piezo-charges. The piezo-charges may produce mirror charges at the meal side. The positive piezocharges effectively may lower the barrier height at the local Schottky contact, while the negative piezo-charges increase the barrier height (Fig. 1.5(b) and (c)). The role played by the piezopotential is to effectively change the local contact characteristics through an internal field depending on the crystallographic orientation of the material and the sign of the strain, thus, the charge carrier transport process is 1 Introduction of Piezotronics and Piezo-Phototronics





tuned/gated at the M–S contact. Therefore, the charge transport across the interface can be largely dictated by the created piezopotential, which is the gating effect. With considering the change in piezopotential polarity by switching the strain from tensile to compressive, the local contact characteristics can be tuned and controlled by the magnitude of the strain and the sign of strain. These are the cores of the piezotronic effect.

#### **1.5.2** Piezotronic Effect on p-n Junction

When a p-type and a n-type semiconductors form a junction, the holes in the ptype side and the electrons in the n-type side tend to redistribute to balance the local potential, the interdiffusion and recombination of the electrons and holes in the junction region forms a charge depletion zone. The presence of such a carrier-free zone can significantly enhance the piezoelectric effect, because the piezo-charges will be mostly preserved without being screened by local residual free carriers. As shown in Fig. 1.5(d), for a case that the p-type side is piezoelectric and a strain is applied, local net negative piezo-charges are preserved at the junction provided



**Fig. 1.5** (a)–(c) Energy band diagram for illustrating the effects of piezoelectric polarization charges on a Schottky contacted metal–semiconductor interface without and with the presence of non-mobile, ionic charges at the metal–semiconductor interface. The piezoelectric charges are indicated at the interface. (d)–(f) Energy band diagram for illustrating the effect of piezoelectricity on a p–n junction that is made of two materials of similar bandgaps. The distorted band with the presence of piezoelectric charges is indicated by *red lines* 

the doping is relatively low so that the local free carriers are not enough to fully screen the piezo-charges. The piezopotential tends to raise the local band slightly and introduce a slow slope to the band structure. Alternatively, if the applied strain is switched in sign (Fig. 1.5(e)), the positive piezo-charges at the interface creates a dip in the local band. A modification in the local band may be effective for trapping the holes so that the electron–hole recombination rate can be largely enhanced, which is very beneficial for improving the efficiency of an LED. Furthermore, the inclined band tends to change the mobility of the carriers moving toward the junction.

With the creation of a piezopotential in one side of the semiconductor material under strain, the local band structure near the p–n junction is changed/modified. For



**Fig. 1.6** Energy band diagram for illustrating the effect of piezoelectricity on a p–n junction that is made of two materials of similar bandgaps. The band diagrams for the p–n junction with and without the presence of piezoelectric effect for the four possible cases are shown using *dark* and *red curves*, respectively. The bandgap for the n-type and p-type are assumed to be about equal. The effect of reversal in polarity is presented

easy understanding, we include the screening effect of the charge carriers to the piezopotential in the discussion, which means that the positive piezopotential side in n-type material is largely screened by the electrons, while the negative piezopotential side is almost unaffected. By the same token, the negative piezopotential side in p-type material is largely screened by the holes, but leaves the positive piezopotential side almost unaffected. As shown in Fig. 1.6(b) for a case that the p-type side is piezoelectric and a strain is applied, the local band structure is largely changed, which significantly affects the characteristic of charge carriers flow through the interface. This is the core of the piezotronic effect.

In addition, the holes on the p-type side can drift to the n-type side to combine with the electrons in the conduction band, possibly resulting in an emission of photon. This is a process of piezopotential induced photon emission, e.g., *piezophotonics*. The following conditions may need to be met in order to observe the piezophoton tonic process. The magnitude of the piezopotential has to be significantly large in comparison to  $\phi_i$ , so that the local piezoelectric field is strong enough to drive the diffusion of the holes across the p–n junction. The straining rate for creating the piezopotential has to be rather large, so that the charge carriers are driven across the interface within a time period shorter than the time required for charge recombina-



tion. The width of the depletion layer has to be small so that there are enough charge carriers available in the acting region of the piezopotential. Finally, a direct bandgap material is beneficial for the observation of the phenomenon.

The fundamental working principles of the p–n junction and the Schottky contact are that there is an effective barrier that separates the charge carriers at the two sides to across. The height and width of the barrier are the characteristic of the device. In piezotronics, the role played by the piezopotential is to effectively change the width of p–n junction or height of SB by piezoelectricity.

## 1.6 Piezo-Phototronic Effect

Piezophototronics was first coined in 2010 [24–26]. For a material that simultaneously has semiconductor, photon excitation and piezoelectric properties, besides the well-known coupling of semiconductor with photon excitation process to form the field of optoelectronics, additional effects could be proposed by coupling a semiconductor with piezoelectric to form a field of piezotronics, and piezoelectric with photon excitation to form a field of piezophotonics. Furthermore, a coupling among semiconductor, photon excitation and piezoelectric is a field of *piezo-phototronics*, which can be the basis for fabricating piezo-photonic–electronic nanodevices. The *piezo-phototronic effect* is to use the piezopotential to tune/control the charge generation, separation, transport and/or recombination at an interface/junction for achieving superior optoelectronic processes (Fig. 1.7).

#### 1.7 One-Dimensional Wurtzite Nanostructures for Piezotronics

The principles illustrated for piezotronics and piezo-phototronics apply to both of thin film and NWs. But the NWs are of great advantageous than thin films for the following reasons. First, ZnO NWs can be grown using a chemical approach at low temperature (<100 °C) on any substrate and any shape substrate, exhibiting a huge advantage for scaling up at a low cost; while it is practically difficult to make high quality single crystal thin film at low temperature. Secondly, owing to the largely reduced size, NWs exhibit extremely high elasticity that allows large degrees of mechanical deformation (up to 6 % in tensile strain according to theoretical calculation for very small wire [27]) without cracking or fracture, while thin film can easily generate cracks after applying even smaller strain. Third, the small size of the NWs largely increases the toughness and robustness of the structure so that it is almost fatigue free. Fourth, a relatively small force is required to induce the mechanical agitation, so that it can be very beneficial for building ultrasensitive devices. Finally, NWs may exhibit higher piezoelectric coefficient than thin film [28].

One-dimensional nanomaterials, such as nanowires and nanobelts, are ideal for piezotronics and piezo-phototronics, because they can tolerate a large mechanical strain. ZnO, GaN, InN and possibly doped PZT materials are potential candidate for piezotronics. Currently, the most popular structure is ZnO NWs for three main reasons. First, ZnO NWs can be easily grown at a large quantity using vapor-solid process or chemical approach at low temperature. Secondly, they are biological compatible and environmentally friendly. Finally, they can be grown on substrate and any shape substrate. The vapor-solid growth usually takes place in a tube furnace by vaporizing ZnO powders with the presence of carbon at a temperature of ~900 °C. Patterned growth is possible with the introduction of Au catalyst. Pulse laser deposition (PLD) can be used for NW growth. A KrF excimer laser (248 nm) was used as the ablation source to focus on a ceramic target, which is a stack of ZnO powder. A control of pressure can give nice NW array (Fig. 1.8(a)).

The most commonly used chemical agents for the hydrothermal synthesis of ZnO NWs are zinc nitrate hexahydrate and hexamethylenetetramine [29, 30]. Zinc nitrate hexahydrate salt provides  $Zn^{2+}$  ions, required for building up ZnO NWs. Water molecules in the solution provide  $O^{2-}$  ions. Even though the exact function of hexamethylenetetramine during the ZnO NW growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and grad-ually produce  $OH^-$ . This is critical in the synthesis process because, if the hexamethylenetetramine hydrolyzes very fast and produces a lot of  $OH^-$  in a short period of time, the  $Zn^{2+}$  ions in solution would precipitate out very quickly due to the high pH environment. Using a pattern generated by laser interference, well aligned NW arrays have been grown at a temperature around 85 °C (Fig. 1.8(b)).

NWs grown by vapor phase technique at high temperature usually have low defects and they are most adequate for studying piezotronic and piezo-phototronic effects [31, 32]. A treatment in oxygen plasmon can effectively reduce the vacancy concentration. The low-temperature chemically grown NWs have a relatively high concentration of defects, and they are most useful for piezoelectric nanogenerators.

**Fig. 1.8** ZnO nanowire arrays grown by (**a**) pulse laser deposition technique and (**b**) low-temperature solution based approach



### **1.8 Perspective**

Today's electronics and optoelectronics are mostly based on Si, II–VI and III–V compound semiconductor materials, with focuses on CMOS technology, LED, photon detector and solar cell. Piezoelectricity, on the other hand, relies on PZT type of provskite materials, which are rarely used for electronics and optoelectronics. Owing to the gigantic difference in materials systems, the overlap between piezoelectricity and optoelectronics is rather limited. With the use of wurtzite materials, such as ZnO, GaN and InN, which simultaneously have piezoelectric and semiconductor properties, we have coupled piezoelectricity with optoelectronic excitation processes and coined a few new fields (Fig. 1.9). The core relies on piezopotential that is created in a piezoelectric material by applying a stress, and it is generated by the polarization of ions in the crystal. *Piezotronics* is about the devices fabricated using the piezopotential as a "gate" voltage to tube/control charge carrier transport at a contact or junction. *Piezo-phototronic effect* is to use the piezopotential to control the carrier generation, separation, transport, and/or recombination for improving the performance of optoelectronic devices, such as photon detector, solar cell and LED.

Z.L. Wang's group has devoted over 12 years for studying ZnO nanostructures and its wide range of applications. Our systematic studies and the field coined can



Fig. 1.9 Potential and perspective applications of piezotronics, piezo-phototronics, and nanogenerators [6], which are important future directions and fields in near future. *Middle*: schematic diagram showing the three-way coupling among piezoelectricity, photoexcitation and semiconductor, which is the basis of piezotronics (piezoelectricity–semiconductor coupling), piezophotonics (piezoelectric–photon excitation coupling), optoelectronics, and piezophototronics (piezoelectricity–semiconductor–photoexcitation)

be summarized using a "tree" structure, as shown in Fig. 1.10. The fundamental "root" of all these fields is: piezopotential and semiconductor as the basic physics, and wurtzite structure as the fundamental materials system; the "branches" are the fields we have coined; and the "fruits" are the important applications. Furthermore, fundamental quantum phenomena possibly arising from nano-scale piezo-physics can be explored in near future. Besides the wurtzite family, we have doped provskite type structures, such as PZT, BaTiO<sub>3</sub>, for such studies.

Piezotronics is likely to have important application in sensors, human-silicon technology interfacing, MEMS, nanorobotics and active flexible electronics. The role played by piezotronics in interfacing human–CMOS technology is similar to the mechanosensation in physiology. Mechanosensation is a response mechanism to mechanical stimuli. The physiological foundation for the senses of touch, hearing and balance, and pain is the conversion of mechanical stimuli into neuronal signals. We anticipate near future applications of piezotronics and piezo-phototronics in sensor network, bioscience, human–machine interfacing and integration, and energy sciences.



**Fig. 1.10** A "tree" idea for summarizing the fields of nanogenerator, hybrid cell for harvesting multi-type energies [33–36], self-powered system [6], piezotronics, piezo-phototronics and possibly piezophotonics that have been developed by Wang's group in the last decade. The fundamental "root" of all these fields is: piezopotential and semiconductor as the basic physics, and ZnO as the fundamental materials system. All of the fields are derived based on these basics

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