Investigation of the dynamic properties of on-chip coupled piezo/photodiodes by time-resolved atomic force and Kelvin probe microscopy

Cite as: AIP Advances 10, 105121 (2020); https://doi.org/10.1063/5.0028481
Submitted: 04 September 2020 . Accepted: 27 September 2020 . Published Online: 13 October 2020

Willemijn M. Luiten, Verena M. van der Werf, Noureen Raza, and Rebecca Saive

COLLECTIONS

Paper published as part of the special topic on Chemical Physics, Energy, Fluids and Plasmas, Materials Science and Mathematical Physics

ARTICLES YOU MAY BE INTERESTED IN

Progress and perspective on polymer templating of multifunctional oxide nanostructures
Journal of Applied Physics 128, 190903 (2020); https://doi.org/10.1063/5.0025052

Atomic force microscopy: Emerging illuminated and operando techniques for solar fuel research
The Journal of Chemical Physics 153, 020902 (2020); https://doi.org/10.1063/5.0009858

Tracking ferroelectric domain formation during epitaxial growth of PbTiO$_3$ films
Applied Physics Letters 117, 132901 (2020); https://doi.org/10.1063/5.0021434
Investigation of the dynamic properties of on-chip coupled piezo/photodiodes by time-resolved atomic force and Kelvin probe microscopy

Willemijn M. Luiten, Verena M. van der Werf, Noureen Raza, and Rebecca Saive

AFFILIATIONS
MESA+ Institute for Nanotechnology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands

ABSTRACT
We have studied the dynamic properties of hybrid devices in which the piezoelectric material lead zirconate titanate is integrated with silicon photodiodes on-chip. Such an integrated system enables direct conversion of light energy into mechanical deformation and motion, opening up new pathways for light propulsion in microrobots and nanorobots. By operating our devices under alternating illumination and simultaneously recording the time-dependent deformation and surface potential, we were able to derive frequency and voltage dependent time constants and phase relations between photovoltage and deformation. We observed that the silicon top contact resistance limits the response time to 6 ms in small area devices in which the capacitance is low. Furthermore, we observed a phase transition at low frequency that seems to be consistent with the occurrence of a negative capacitance. Our method of using time-dependent atomic force and Kelvin probe force microscopy proves to be suitable for the investigation of nanoscale, dynamic properties of light-driven piezo systems and can lead the design of next generation devices.

Using light as an energy source offers numerous advantages, with low-loss and wireless transport being two key factors, often leveraged by allowing power conversion to occur at the location where the power is needed. Recently, these advantages have been used in light-driven microrobots and nanorobots, such as Feringa’s molecular machines, photoresponsive soft microrobots, and several others. In existing systems, it can be difficult to control the direction of the motion, and often, the system relies on a certain operation environment. One way to tackle these shortcomings is to take advantage of a highly versatile semiconductor and nanofabrication tool sets. Radio frequency microcircuits and photodiodes have been discussed to provide energy for light propulsion, and piezoelectric materials have been used for precise motion control. The combination of these ideas, a photodiode coupled with piezoelectric materials, allows using light as a versatile energy source to create an electric field that results in deformation of the piezoelectric material.

Here, we present time-resolved atomic force microscopy (AFM) in combination with time-resolved Kelvin probe force microscopy (KPFM) as a promising method to investigate the interplay between electrical and mechanical behaviors on the nanoscale of photovoltage-driven piezo devices. Kelvin probe microscopy has previously been shown to provide accurate information on the spatially resolved and time-resolved photovoltage of solar cells. Contrary to an external measurement with an oscilloscope, Kelvin probe has the strong advantage that it provides the local voltage at the device surfaces, without external wires and contacts influencing the magnitude or response time of the signal.

First, we fabricated devices in which the piezoelectric material lead zirconate titanate (PZT) is coupled with silicon photodiodes on-chip [Figs. 1(a) and 1(b)], and subsequently, we investigated the frequency and voltage dependent displacement and (photo)voltage of piezo-photomotion devices under alternating illumination or electrical bias. With our method, it is
possible to determine the response time and the phase shift between the photovoltage and the mechanical response. Overall, our study shows that a combination of time-dependent AFM and KPFM measurements provides valuable information on the dynamic microscopic device properties and can guide the design of next generation device architectures.

A schematic of the top view and the cross section of the fabricated structures are shown in Fig. 1(a). Patterned silicon p–n junctions were created by boron diffusion in one-side polished n-doped silicon (001) wafers. Diffusion was performed through deposition [plasma enhanced chemical vapor deposition (PECVD)] and patterning of boron doped SiO2, followed by annealing for 30 min at 1100 °C. A stack of 60 nm lanthanum nickelate (LNO), 930 nm lead zirconia titanate (PZT), and 120 nm LNO was deposited by pulsed laser deposition and subsequently patterned by photolithography and a three step wet etching process with buffered HF for PZT and 18% HCl for LNO. To prevent shunting of the photovoltage present at the top contact is determined as the difference between CPD in the dark and under illumination. 14–16 It has been previously shown that neither an externally applied voltage nor the photovoltage interferes with the topography measurements in AM, single or dual pass KPFM, neither for inorganic nor for organic solar cells or light emitting diodes14–16 as long as the CPD is fully compensated.22 In accordance with this, for solar cells without PZT, we did not measure any displacement beyond the noise level (see S6 in the supplementary material). Spatial images were taken at a scan size of 10 nm in order to not be influenced by local surface variations. The displacement was measured during the topography measurement, and the CPD voltage was measured in the lift mode. For the lift scan, the tip was raised by 92 nm and an AC driving voltage of 500 mV was applied at the resonance frequency of the cantilever (∼75 kHz). An example CPD scan for trace and retrace can be found in Fig. S4.1 of the supplementary material. The line scans were transformed into temporal data using the scan frequency of the AFM. To make sure that no additional dwell time offsets the onset of the dual pass, the experiment was conducted under different scan rates and frequencies, and it was concluded that no dwell time was present. The measurements reported in this paper were conducted under a scan rate of fscan = 0.976 563 Hz for most measurements and fscan = 0.209 Hz for measurements at low frequency, labeled low scan rate in Fig. 4(b). In Fig. 4(b), it can be seen that phase results for measurements under alternating illumination at the higher scan rate of fscan = 0.976 563 Hz were slightly offset against the trend of the other measurements (both at fscan = 0.976 563 Hz and at fscan = 0.209 Hz). We attribute this effect to an altered contact resistance caused by remounting and reconnecting of the sample for emission SEM using the in-lens detector, at an acceleration voltage of 1.4 kV and a probe current of 141 pA.

Computational simulations of the voltage dependent device deformation were performed by finite element analysis with COMSOL Multiphysics version 5.5. We used the piezoelectric device module, which combines solid mechanics physics and electrostatic physics to create the piezoelectric effect. The simulated model consists of four layers in total, with the silicon substrate being the first material, followed by the first LNO electrode (100 nm), PZT (1 μm), and the second LNO electrode (100 nm). For silicon and PZT, we used material parameters as implemented in COMSOL (PZT: PZT-5H); for LNO, we obtained material properties from Ref. 19. In solid mechanics, two material models were applied, the linear elastic material (on substrate and electrode domains) and the piezoelectric material (on the piezoelectric domain) models. Furthermore, a fixed constraint was applied on the bottom edges of the silicon substrate to model displacement endpoints. In the electrostatic module, a positive potential difference was applied between top and bottom electrodes to examine the induced deformation. Subsequently, a user-controlled mesh was created with a maximum node size of 0.2 mm and minimum element size of 0.002 mm.

Time-dependent height and contact potential difference (CPD) measurements were performed with a Bruker scanning probe microscope. The system was operated in the tapping (AC) atomic force microscopy (AFM) mode, and the CPD was measured in the amplitude modulated (AM) dual pass Kelvin probe force microscopy (KPFM) mode. A topography and line profile measured on top of LNO can be found in Fig. S3.1 of the supplementary material. The voltovoltage present at the top contact is determined as the difference between CPD in the dark and under illumination. 14–16 It has been previously shown that neither an externally applied voltage nor the photovoltage interferes with the topography measurements in AM, single or dual pass KPFM, neither for inorganic nor for organic solar cells or light emitting diodes14–16 as long as the CPD is fully compensated.22 In accordance with this, for solar cells without PZT, we did not measure any displacement beyond the noise level (see S6 in the supplementary material). Spatial images were taken at a scan size of 10 nm in order to not be influenced by local surface variations. The displacement was measured during the topography measurement, and the CPD voltage was measured in the lift mode. For the lift scan, the tip was raised by 92 nm and an AC driving voltage of 500 mV was applied at the resonance frequency of the cantilever (∼75 kHz). An example CPD scan for trace and retrace can be found in Fig. S4.1 of the supplementary material. The line scans were transformed into temporal data using the scan frequency of the AFM. To make sure that no additional dwell time offsets the onset of the dual pass, the experiment was conducted under different scan rates and frequencies, and it was concluded that no dwell time was present. The measurements reported in this paper were conducted under a scan rate of fscan = 0.976 563 Hz for most measurements and fscan = 0.209 Hz for measurements at low frequency, labeled low scan rate in Fig. 4(b). In Fig. 4(b), it can be seen that phase results for measurements under alternating illumination at the higher scan rate of fscan = 0.976 563 Hz were slightly offset against the trend of the other measurements (both at fscan = 0.976 563 Hz and at fscan = 0.209 Hz). We attribute this effect to an altered contact resistance caused by remounting and reconnecting of the sample for
measured photovoltage showed approximately a square wave signal followed approximately a sine behavior (fitted in black), whereas the curves) and photovoltage (orange curves) are shown upon alternation of illumination, i.e., turning the LEDs on and off at a frequency of several nm can be expected. Nevertheless, the actual properties of our devices should fall within the simulated range, which shows that a maximum displacement of 210 pm V\(^{-1}\) was reported. In the wafer scale growth used in this study, Nguyen et al. obtained a \(d_{33}\) of 210 pm V\(^{-1}\). With a photovoltage of 300 mV, one would expect a height difference of 63 pm. However, this response is enhanced by curving of the wafer due to the contraction of the material transverse to the electric field caused by the transverse piezoelectric coefficient \(d_{33}\) and hence, we can expect to measure a significantly higher displacement. This is schematically shown in Fig. 1(b). Figure 2(a) shows the simulated location dependent displacement of the top surface with 1 V applied to PZT. The size of the silicon chip was \(10 \times 10 \, \text{mm}^2\) with a thickness of 50 \(\mu\)m, and the PZT layer was \(6 \times 6 \, \text{mm}^2\) wide, 1 \(\mu\)m thick, and positioned in the lower left corner. The location dependent displacement strongly depends on the device geometry. In Fig. 2(b), the maximum displacement is shown as a function of silicon chip thickness and size with a constant PZT width of \(6 \times 6 \, \text{mm}^2\) and thickness of 1 \(\mu\)m. In our experiments, both the thickness and the chip size and shape showed significant variation and sometimes irregular shapes, such that an exact prediction of the displacement is difficult. Per design, the chip size varied from device to device as can be seen in S1 in the supplementary material and, furthermore, was slightly altered from the layout during dicing. In addition, pillars remaining on the rear surfaces of our membranes as explained in S2 in the supplementary material likely influenced the membrane behavior. Nevertheless, the actual properties of our devices should fall within the simulated range, which shows that a maximum displacement of several nm can be expected.

In Fig. 3, the measured time-dependent displacement (blue curves) and photovoltage (orange curves) are shown upon alternating illumination, i.e., turning the LEDs on and off at a frequency of 1 Hz [Fig. 3(a)] and 2 Hz [Fig. 3(b)]. The measurements were performed by AFM and KPFM as explained above. The displacement followed approximately a sine behavior (fitted in black), whereas the measured photovoltage showed approximately a square wave signal (fitted in red). This behavior suggests a driven mechanical oscillation contrary to a quasi-static behavior in which the displacement should also reach a plateau. Furthermore, the photovoltage deviates from a perfect square wave signal and can be fitted as resistor–capacitor (RC) charging and discharging events. From the slope of the discharging, the RC constant can be determined by using the relation \(V(t) = V_{\text{ext}} \times e^{-t/\tau}\), where \(V_{\text{ext}}\) is the externally applied voltage. Within the range of 0.4 V–1.6 V externally applied voltage, the RC time constant remained constant within the errors at a value of 6.0 ± 0.5 ms. To shed light on the origin of this RC constant, we also performed measurements of samples with different PZT areas. The
area dependent RC constants are plotted in Fig. 4(a). To separate the R and C components, we calculated the capacitance that is expected from the LNO/PZT/LNO structure where we assume LNO to act as the capacitor plates and PZT as the dielectric with a relative dielectric permittivity of $1850 \pm 50$. Subsequently, the resistance was derived from the measured time constant together with the calculated capacitance. The area dependent R and C components can be found in Fig. 4(a). It is striking that the R component shows an inverse area dependence. Compared with the device structure shown in Fig. 1(a), the only resistance being dependent on the LNO/PZT/LNO area is the contact resistance between silicon and LNO. Assuming this contact to be the major cause for series resistance, we obtain a contact resistance of $4.0 \pm 0.4 \text{k}\Omega/\text{cm}^2$, an understandably high value as we did not pay attention to optimize this contact. There is a tradeoff area between R and C components at which the time constant is lowest. Moving forward, we plan to focus on small area, micrometer or sub-micrometer devices, which will keep the capacitance low but shows the strong need for optimized contact layers.

Coming back to Fig. 3, a phase difference between the photovoltage and the displacement signal can be seen. For 1 Hz [Fig. 3(a)], the displacement rises in phase with the photovoltage, while for 2 Hz [Fig. 3(b)], the displacement is shifted by $\sim 180^\circ$. We determined this phase difference at different frequencies and both with illumination and with external bias provided by a function generator. The frequency dependent phase shift is shown in Fig. 4(b). The phase shift slightly increases with the increasing frequency, but there is a sudden step of $\sim 180^\circ$ at around 1.5 Hz. Such a phase change reminds of the behavior of a driven harmonic oscillator with driving frequency changing from below the resonance to above the resonance. We concluded already above that the sine behavior of the measured displacement suggests a driven harmonic mechanical oscillation. However, the mechanical resonance frequency of such structures is usually significantly higher than 1.5 Hz, and we calculated a
resonance frequency of ~250 Hz when approximating our structure as a clamped square plate. In addition, the charging time of the photovoltage reported above suggests that electrical circuit resonances might be present. We excluded the possibility of a resistor, capacitor, inductor (RCL) circuit as discussed in S5.

A different model fits our observation better, namely, the transition from a negative to a positive capacitance. Such a behavior has been frequently observed in semiconductor devices and has been explained by non-ideal semiconductor/metal interfaces through the discharge of trap states at the interface. In Fig. 5(a), the calculated time-dependent voltages across the solar cell capacitor (silicon/LNO interface) and across the LNO/PZT/LNO capacitor are shown if we assume an electrical circuit as shown in the inset in which the capacitances can be either negative or positive. For the LNO/PZT/LNO capacitance (C_PZT), 58 µF is used as calculated above. The capacitance of the silicon/LNO interface (C_solar) is changed between ~50 µF and 80 µF. With a negative capacitance, discharging would be observed across the solar cell capacitor, which is in line with the theory of trap states filling and unfilling at the interface. In Fig. 5(b), the calculated phase behavior is shown for the circuit in the inset of Fig. 5(a) with (blue curve) ~50 µF capacitance of C_solar and (orange curve) 80 µF of C_solar. This model describes our data well with a sudden transition from a negative to a positive capacitance at around 1.5 Hz. While other causes for the phase behavior are certainly possible, the high contact resistance of 4.0 ± 0.4 kΩ/cm² derived from the RC constants makes it likely that this interface has a strong contribution to the temporal behavior of our devices. We conclude that the interface design of on-chip coupled piezo/photodiode devices is crucial to improve the response time.

In summary, we have demonstrated the on-chip integration of the piezoelectric material PZT with silicon photodiodes and we have analyzed the light-induced displacement of such piezo-photonon devices. Enabled by time-resolved AFM and KPFM, we have determined voltage, frequency, and area dependent displacement, RC time constants, and phase shifts. Compared to measuring the photovoltage with wires, this method provides spatially resolved information in the nanoscale without influencing the behavior through connection of wires. We concluded that the poor contact resistivity at the silicon/LNO interface limits the response time for small area samples and needs to be improved in future devices. Furthermore, we observed a phase transition at low frequency that seems to be consistent with a transition from a negative to a positive capacitance. Such a transition has previously been related to poor interfaces in photovoltaic devices and is therefore in agreement with our observation of 4.0 ± 0.4 kΩ/cm² contact resistance at the silicon/LNO interface. Overall, our study shows that the combination of time-dependent AFM and KPFM is a valuable method for the investigation of dynamic properties of photovoltage-driven actuators at the nanoscale and can lead the design of next generation devices.

The supplementary material contains detailed information on the device layout, membrane etching, topography, CPD measurements, and the hypothesis test for an RCL circuit.

The authors acknowledge M. J. de Boer, C. M. Bruinink, and R. R. Wijn for help with establishing the clean room process flow as well as the staff and researchers of the MESA+ Institute for their support with device fabrication, in particular D. M. Nguyen, C. A. M. Harteveeld, H. van Vossen, R. R. Wijn, P. W. C. Linders, R. Wolf, M. P. Nijhuis, and M. A. Smithers (SEM). Furthermore, the authors thank H. Bakker for AFM training and Yorick Birkhölzer and Guus Rijnders for helpful discussions.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. G. Marx, Nature 211(5044), 22 (1966).
2. J. Yang, C. Zhang, X. Wang, W. Wang, N. Xi, and L. Liu, Sci. China: Technol. Sci. 62(1), 1–20 (2019).
3 P. Khulbe, Int. J. Pharm. Sci. Res. 5(6), 2161–2173 (2014).
4 R. A. Van Delden, M. K. J. Ter Wiel, M. M. Pollard, J. Vicario, N. Koumura, and B. L. Feringa, Nature 437(7063), 1337 (2005).
5 S. Palagi, A. G. Mark, S. Y. Reigh, K. Melde, T. Qiu, H. Zeng, C. Parmeggiani, D. Martella, A. Sanchez-Castillo, N. Kapernaum, F. Giesselmann, D. S. Wiersma, E. Lauga, and P. Fischer, Nat. Mater. 15(6), 647 (2016).
6 H. Zeng, P. Wasylczyk, C. Parmeggiani, D. Martella, M. Burresi, and D. S. Wiersma, Adv. Mater. 27(26), 3883–3887 (2015).
7 B. Dai, J. Wang, Z. Xiong, X. Zhan, W. Dai, C.-C. Li, S.-P. Feng, and J. Tang, Nat. Nanotechnol. 11(12), 1087 (2016).
8 S. Lu and B. Panchapakesan, Nanotechnology 16(11), 2548 (2005).
9 Y. Mita, N. Sakamoto, N. Usami, A. Frappé, A. Higo, B. Stefanelli, H. Shiomi, J. Bourgeois, and A. Kaiser, Sens. Actuators, A 275, 75–87 (2018).
10 S. Chalasani and J. M. Conrad, paper presented at the IEEE SoutheastCon 2008, 2008.
11 K. A. Cook-Chennault, N. Thambi, and A. M. Sastry, Smart Mater. Struct. 17(4), 043001 (2008).
12 S. Mekid, S. Bashmal, and H. M. Ouakad, Recent Pat. Nanotechnol. 10(1), 44–58 (2016).
13 J. Toledo, V. Ruiz-Diez, A. Díaz-Molina, D. Ruiz, A. Donoso, J. C. Bellido, E. Wistrela, M. Kucera, U. Schmidt, and J. Hernando-García, paper presented at the Actuators, 2017.
14 V. W. Bergmann, S. A. Weber, F. J. Ramos, M. K. Nazeeruddin, M. Grätzel, D. Li, A. L. Domanski, I. Lieberwirth, S. Ahmad, and R. Berger, Nat. Commun. 5, 5001 (2014).
15 R. Saive, M. Scherer, C. Mueller, D. Daune, J. Schinke, M. Kroeger, and W. Kowalsky, Adv. Funct. Mater. 23(47), 5854–5860 (2013).
16 R. Saive, C. Mueller, J. Schinke, R. Lovrincic, and W. Kowalsky, Appl. Phys. Lett. 103(24), 243303 (2013).
17 L. Collins, M. Ahmad, J. Qin, Y. Liu, O. S. Ovchinnikova, B. Hu, S. Jesse, and S. V. Kalinin, Nanotechnology 29(44), 445703 (2018).
18 M. Tanimoto and O. Vatel, J. Vac. Sci. Technol., B 14(2), 1547–1551 (1996).
19 S. Masys and V. Jonauskas, Comput. Mater. Sci.: A 108, 153–159 (1996).
20 C. S. Weigel, W. Kowalsky, and R. Saive, Phys. Status Solidi RRL 9(8), 475–479 (2015).
21 R. Saive, H. Emmer, C. T. Chen, C. Zhang, C. Honsberg, and H. Atwater, IEEE J. Photovoltaics 8(6), 1568–1576 (2015).
22 S. Guo, S. V. Kalinin, and S. Jesse, Nanotechnology 23(12), 125704 (2012).
23 M. D. Nguyen, E. P. Houwman, H. Yuan, B. J. Wylie-van Eerd, M. Dekkers, G. Koster, J. E. Ten Eshof, and G. Rijnders, ACS Appl. Mater. Interfaces 9(41), 35947–35957 (2017).
24 M. Nguyen, R. Tiggelaar, T. Aukes, G. Rijnders, and G. Roelof, J. Phys.: Conf. Ser. 922, 012022 (2015).
25 M. D. Nguyen, E. P. Houwman, M. Dekkers, and G. Rijnders, ACS Appl. Mater. Interfaces 9(11), 9849–9861 (2017).
26 W. Heywang, K. Lubitz, and W. Wersing, Piezoelectricity: Evolution and Future of a Technology (Springer Science + Business Media, 2008).
27 M. Safizadeh, I. M. Darus, and M. Mailah, paper presented at the 2010 International Conference on Intelligent and Advanced Systems, 2010.
28 X. Wu, E. S. Yang, and H. L. Evans, J. Appl. Phys. 68(6), 2845–2848 (1990).
29 M. Ershov, H. C. Liu, L. Li, M. Buchanan, Z. R. Wasilewski, and A. K. Jonscher, IEEE Trans. Electron Devices 45(10), 2196–2206 (1998).
30 Panigrahi, R. Vandana, R. Singh, N. Batra, J. Gope, M. Sharma, P. Pathi, S. K. Srivastava, C. M. S. Rauthan, and P. K. Singh, Sol. Energy 136, 412–420 (2016).