Pressure-assisted fabrication of perovskite light emitting devices

Cite as: AIP Advances 11, 025112 (2021); https://doi.org/10.1063/5.0035953 Submitted: 03 December 2020 . Accepted: 06 January 2021 . Published Online: 05 February 2021

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ABSTRACT

This paper presents the results of pressure-effects on performance characteristics of near-infra-red perovskite light emitting diodes (PeLEDs) using a combination of experimental and analytical/computational approaches. First, pressure-effects are studied using models that consider the deformation and contacts that occur around interfacial impurities and interlayer surface roughness in PeLEDs. The predictions from the model show that the sizes of the interfacial defects decrease with increasing applied pressure. The current–voltage characteristics of the fabricated devices are also presented. These show that the PeLEDs have reduced turn-on voltages (from 2.5 V to 1.5 V) with the application of pressure. The associated pressure-induced reductions in the defect density and the bandgaps of the perovskite layer are then used to explain the improved performance characteristics of the PeLED devices.

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I. INTRODUCTION

Organic–inorganic lead halide-based perovskite electronic materials have attracted significant attention in the recent years.^{1–5} This is due to the attractive optical and electrical performance of perovskite solar cells and perovskite light emitting diodes (PeLEDs).^{3–8} Perovskite materials are attractive because they can be easily solution processed^{5–7} without any high temperature heating.^{5,8–10} They also possess tunable optical bandgaps in the visible regime, which makes them promising materials for optoelectronic applications.^{5,11}

Several efforts have been made to improve the efficiency of the hybrid perovskite-based electronic systems. $^{12-14}$ These include

film morphology,^{15,16} interface engineering,^{12,13} and modifications on methods of fabrication.^{3,12,14} Starting with the liquid electrolyte configurations of the organic–inorganic halides CH₃NH₃PbI₃, the efficiency of 3.8% was presented for solar cells by Kojima *et al.*¹⁷ This was later improved by Im *et al.*¹⁸ to 6.5%. Further improvements on the stability and modification of architecture have facilitated rapid growth in the efficiency of perovskite solar cells, which has risen from the 3.8% to above 25%, within a decade of intensive research.^{12–14,17–19}

Organometallic perovskites have also been shown to have significant potential for applications in light emitting diodes.^{5,8,20} Perovskite materials have strong photoluminescent (PL) properties and exhibit size independent high color purity,^{21,22} which make them to be good candidates for applications in emitters.⁵ Their high color purity has also made them attractive alternatives to conventional organic and inorganic light emitters.

In an effort to produce PeLEDs, the first 3D perovskite emitters were made by Kojima *et al.*,¹⁷ after the failure of their prior attempts^{23,24} to fabricate light emitting devices with related perovskite materials. The initial work of Tan *et al.*⁵ resulted in the first infrared and visible perovskite light emitting diodes with potential applications in display technologies. Since then, significant work has been done to explore different processing methods^{8,20} and layered architectures for the fabrication of perovskite light emitting diodes with attractive combinations of improved efficiency in photoluminescent (PL) and electroluminescent (EL) with good stability.^{7,20}

Several methods have been used to improve the performance of the PeLEDs. These include the processing condition,^{7,20} modification, and optimization of layered architectures.^{5,15} For instance, Cho et al.⁷ have been able to suppress the challenges of exciton quenching by using excess methyl-ammonium bromide (MABr) while synthesizing the methyl-ammonium lead-bromide (CH₃NH₃PbBr₃) solution. This is to reduce the presence of metallic lead (Pb), which is usually a problem as it restricts the efficiency of PeLEDs. The presence of metallic lead is due to accidental losses of bromine atoms or incomplete reactions between MABr and lead bromide (PbBr₂).²⁵ The resulting excess Pb decreases the rate of radiative recombination.²⁶ In addition, Yu et al.²⁷ have used amine-based solvent treatment as surface modifiers between TiO₂ and the perovskite layer. This enhances electron injection and hole blocking. It also ensures a uniform morphology, devoid of metal oxide defects or pin holes, and energy barrier mismatch.

Interestingly, pressure has also been considered as a key parameter that can be used to enhance optoelectronic systems.^{28–32} The application of pressure (both hydrostatic and nonhydrostatic) to perovskite layers also influences their molecular packing and structure.^{30–33} Furthermore, increased pressure on perovskite materials induces crystallization due to the reduction in bonding length,^{34,35} which can later cause amorphization at higher pressures.^{33,36,37} Hence, pressure-induced crystallization enhances the structural, electronic, and optical properties of multilayered perovskite structures.^{31–33} Amorphization can also occur due to the rearrangement of the atoms.^{33,36,37} Oyelade *et al.*³³ have shown that remotely applied pressures on perovskite solar cells can reduce interfacial defects and induce higher stress at defect sites, which can cause induced crystallization. However, the potential effects of pressure on pre-existing defects (within the layered architecture of PeLEDs) have not been studied in the previous studies. Usually, these defects are unavoidable at regions separating materials that have different crystal structure and/or crystallographic orientations. Here, we use a combination of experimental, computational, and analytical approaches to study pressure-effects on defects, carrier mobility, optical properties, and the performance characteristics of PeLEDs. Following Sec. I, the models for the estimation of adhesion and contact length are presented in Sec. III. The materials and experimental methods are then described in Sec. III, before presenting the results and discussion in Sec. IV. The salient conclusions arising from this study are presented in Sec. V.

II. THEORY OF INTERFACIAL SURFACE CONTACTS

The fabrication of organic, inorganic, and hybrid light emitting diodes involves the layer-by-layer deposition of thin films. The deposition technique can involve solution processing or evaporation. It is important to have good interfacial surface contacts for work function alignment and enhancement between adjacent layers in organic electronic devices.^{38,39} The interfacial contacts can be enhanced by the application of pressure (compression treatment).^{33,39–41} Furthermore, the structure and mechanical properties of thin films (subjected to compression) have a strong effect on the deformation of the films around entrapped dust/impurity particles.^{41,42} These may include trapped particles that can be stiff, semi-rigid, or compliant.^{42,43}

Interfacial surface contacts between thin films can be improved when pressure is applied to deform the upper film to contact the adjacent (bottom) film. The deformation of a thin film around interfacial particles can be idealized by the displacement of a cantilever beam.^{41,42,44} The schematics of the cantilever beam before and after deformation are presented in Figs. 1(a) and 1(b), respectively. As the film deflects, the cantilever meets the adjacent (bottom) layer. Consequently, the cantilever deflections and the interfacial surface contacts between the different adjacent layers can provide insights into the interlayer contacts between layers of the PeLED structures.

However, when the trapped particles between layers are stiff (ITO, MoO₃, TiO₂, quartz, and so on),^{41,42} it may be difficult to achieve significant interfacial layer contacts since the void (defect) length depends on Young's moduli and the heights of the dust particles.^{42,45} If the applied pressure is too much, rigid particles can sink into the compliant adjacent layers and thus induce damage with increased sink-in of trapped particles with a range of diameters.^{42,6,47}

Various analytical models^{27,48,49} have been used to study the contact profiles between thin film interfaces prior to the application of pressure. Figure 1(c) presents the surfaces of films with trapped particles creating defect at the interface. The interfacial defect can be reduced by applying pressure [Fig. 1(d)]. Malyshev and Salganik⁴⁶ considered the contact as the problem of a penny crack subject to bending. They obtained the following relationship between the adhesion energy and the contact profile:

$$\gamma = \frac{2Et^3h^2}{3(1-v^2)r^4},$$
(1)





where E, t, and h are Young's modulus, the thickness of the film, and the height of the blister or trapped particle, respectively; ν is Poisson's ratio of the film material; and γ is the adhesion energy. The relationship between the void length (s) and contact ratio (L_c/L) has been shown to be given by^{41,42,45}

$$s = \left(\frac{3Et^3h^2}{2\gamma}\right)^{\frac{1}{4}} \tag{2}$$

and

$$\frac{L_c}{L} = 1 - \frac{1}{L} \left(\frac{3Et^3 h^2}{2\gamma} \right)^{\frac{1}{4}}.$$
 (3)

The contact length can also be expressed as a function of the applied pressure.^{41,42,46} This gives

$$\frac{L_c}{L} = 1 - \left[\frac{3\left(\frac{E}{1-\nu^2}\right)t^3h}{2PL^4}\right]^{\frac{1}{4}}.$$
(4)

In Eq. (4), L_c is the contact length and P is the applied pressure. This equation has been verified by Akande *et al.*⁴⁸ using experimental studies of adhesion in cold-welded Au–Ag interfaces. Hence, since the material and geometric properties of the thin film layers are known, the contact length, the void lengths, and the adhesion energies (between the various interfaces of the perovskite light emitting devices) can be determined.

III. MATERIALS AND METHODS

A. Experimental methods

1. Fabrication of PeLEDs

The architecture presented in Fig. 2(a) was used for the fabrication of devices. Indium tin oxide (ITO)-coated glass substrates (Sigma Aldrich) were etched carefully using zinc powder and 2M hydrochloric acid (HCl) (Sigma Aldrich). The etched surfaces were mechanically abraded with cotton swabs and washed with deionized water (DI). Subsequently, the etched ITO-coated glass substrates were sequentially cleaned by sonification with Decon 90, DI water, acetone, and isopropyl alcohol (IPA) before blow-drying with nitrogen gas. Further cleaning of the substrates was done in an ultraviolet (UV)-ozone cleaner (Novascan, Main Street Ames, IA, USA) for 20 min to remove any organic contaminants.

A compact titanium oxide (c-TiO₂) was spin-coated onto the cleaned substrates from a 0.3M solution of titanium (diisopropoxide) (75% in isopropanol, Sigma Aldrich) in 1-butanol. The spincoating of c-TiO₂ was carried out for 30 s at 4000 rpm before annealing at 300 °C for 30 min. A mesoporous layer of Al₂O₃ nanoparticles (20 wt.% in isopropanol, Sigma Aldrich) was then spin-coated onto c-TiO₂ at 5000 rpm for 30 s and annealed at 150 °C for 15 min.

A mixed halide perovskite, $CH_3NH_3PbI_{3-x}Cl_x$, was used as the emissive layer. The precursor was prepared by dissolving CH_3NH_3I and $PbCl_2$ (3:1 M ratio) in anhydrous N,N-dimethylformamide (DMF) to give a concentration of 10 wt. %.⁵ The mixture was then stirred at 60 °C for 2 h,²⁶ before it was filtered using



FIG. 2. Schematics of (a) the device architecture and (b) pressure application to PeLEDs that show the device and PDMS anvil before pressure, during press and lift of the anvil.

a 0.45 μ m mesh. The filtered perovskite solution was spin-coated onto Al₂O₃/c-TiO₂/ITO-glass at 3000 rpm for 30 s. This was then annealed at 95 °C for 20 min to form a thin film of perovskite.

poly(3,4-ethylenedioxythiophene)composite of А poly(styrenesulfonate) (PEDOT:PSS) and molybdenum (VI) oxide (MoO₃) was used as a hole transport layer (HTL). This was prepared by dissolving 5 mg of MoO₃ in 1 ml of IPA before blending with PEDOT:PSS in ratio 1:3.50 The solution was deposited onto the emissive layer by spin coating at 4000 rpm for 40 s, followed by annealing at 95 °C for 15 min to remove any residual solvent in the thin film. Finally, a 150 nm thick silver layer was thermally evaporated onto PEDOT:PSS-MoO₃/CH₃NH₃PbI_{3-x}Cl_x/Al₂O₃/c-TiO₂/ITO-glass using an Edwards E306A thermal evaporator (Edwards, Sussex, UK), which was operated at a vacuum of $\sim 10^{-6}$ Torr. The device area of ~ 0.1 cm² was defined using a shadow mask.

To study effects of pressure on the mobility of carrier and the density of trap states caused by the presence of defects in the perovskite film, a single carrier (hole-only) device was fabricated using the structure, ITO/PEDOT:PSS-MoO₃/perovskite/spiro-OMeTAD/Ag. Spiro-OMeTAD was prepared by mixing 72 mg of spiro-OMeTAD, 17.5 μ l of lithium bis (trifluoromethylsulfonyl)imide (Li-FTSI) (Sigma Aldrich) (500 mg in 1 ml of acetonitrile), and 28.2 μ l of 4-tert-butyl pyridine (tBP) (Sigma Aldrich) in 1 ml of chlorobenzene. This was then spin-coated onto the perovskite layer at 5000 rpm for 40 s, while other layers were deposited following the above procedures.

2. Pressure application

First, a PDMS anvil was fabricated from a mixture of Sylgard 184 silicone elastomer (Sylgard 184, Dow Coming) base and Sylgard 184 silicone elastomer curing agent in a volume ratio of 10:1. The mixture was poured into a glass mold of dimension 20 mm \times 20 mm \times 5 mm and then degassed in a vacuum oven for 30 min. This was done to allow all bubbles to disappear at 25 kPa. The degassed PDMS was then cured for 2 h at 60 °C.³⁸

Pressure was then applied on the fabricated PeLEDs using 5848 MicroTester Instron (Instron, Norwood, MA, USA). The configuration of the set is shown in Fig. 2(b). Instron was operated in the compression mode, while its head was set to absolutely ramp at 1.0 mm/min and holds on the devices for 10 min at a pressure of 1 MPa. This procedure was repeated at different pressures between 0 MPa and 12 MPa. All the measurements were obtained under ambient conditions (25 °C).



FIG. 3. FEA model for the pressure treatment in the pressure-assisted fabrication of perovskite light emitting devices: (a) model of the device showing the boundary conditions and (b) mesh density of the model.

3. Material characterization and J-V curves

Both as-prepared and pressure-assisted spin-coated perovskite emitters were characterized. The optical absorbance of the films was measured for the different applied pressures. This was done using an Avantes UV-VIS NIR spectrometer (Avantes, BV, USA), while the microstructures of the films and the cross sections of devices were obtained using a Scanning Electron Microscope (SEM) (JEOL 7000F, JEOL, Inc., MA, USA). The x-ray diffraction patterns of the films were obtained using an x-ray diffractometer (Empyrean, PANalytical, USA) under the Cu K α radiation source with a beta nickel filter at 40 KV and 40 mA. Photoluminescence (PL) spectrum measurements were obtained using the Horiba MicOS microscope optical spectrometer system that consists of a Horiba iHR550 spectrometer, a luminescence microscope with a 50× Edmund Optics Plan Apo NIR Mitutoyo objective, and a Horiba Synapse EM CCD camera. The PL spectrum measurements were then obtained using a single photon counter module (SPD-OEM-VIS, Aurea Technology) and an acquisition software interface.

TABLE I. Mechanical properties of materials for different layers and dust particles.

Materials	Young's modulus (GPa)	Poisson's ratio	References
ІТО	116	0.35	51
TiO ₂	202	0.31	52
Al_2O_3	385	0.3	53
CH ₃ NH ₃ PbI _{3-x} Cl _x	19.77	0.33	33
PEDOT:PSS	1.42	0.3	54
Ag	76	0.48	39 and 53
PDMS	0.0036	0.48	55 and 56
Particle	70	0.3	53

The current-voltage (I–V) curves of the PeLEDs were measured using Keithley Source Meter Unit (SMU) 2400 (Keithley, Tektronix, Newark, NJ, USA). The source meter was operated using the Kickstart software by sweeping voltages between 0 V and 3 V to measure current in the dark. The I–V curves of the asprepared devices were then measured. This procedure was repeated for other devices that were assisted with pressures between 0 MPa and 12 MPa.

B. Computational modeling

The finite element simulations of the effects of pressure on multilayered PeLED structures were carried out using the Abaqus software package (Dassault Systèmes Simulia Corporation, Providence, RI, USA). We considered the segments of the devices in which the region of the embedded particles between electron transporting and photoactive perovskite layers was analyzed in the simulations. For simplicity, axisymmetric geometries (Fig. 3) were used. We assumed that the part of the device, which is farther from the dust particle, has no significant effect on the mechanics around the dust particle.

We used a four-node bilinear axisymmetric quadrilateral element in the mesh. The mesh was dense in the regions near the particle and the contact surfaces. Identical mesh sizes were also used in the regions near the surface contact regimes to ensure convergence in contact simulation. All the materials were assumed to exhibit an isotropic elastic behavior. Young's moduli and Poisson's ratios of the materials for different layers of the PeLEDs are presented in Table I. The bottom of the substrate was fixed to have no displacements and rotations. The outer edge of the model was also fixed to have no lateral movement for continuity, while pressures were applied from the stamp onto the device [Fig. 3(a)]. The mesh density of the model is presented in Fig. 3(b).

IV. RESULTS AND DISCUSSION

A. Interfacial surface contacts

The surface contact lengths between the perovskite layer and the adjacent layers were estimated from Eq. (4) for different applied pressures between 0 MPa and 12 MPa. Figure 4 presents the effects of pressure on the estimated surface contact lengths. The results show that the surface contacts increase with increasing applied pressure.

Figure 4(a) presents the surface contacts for different thicknesses of the perovskite films. The surface contact increases as the thickness of the film decreases with increasing applied pressure. Figure 4(b) presents the effects of pressure on the perovskite film for different sizes of the particle. The results show that, for small particle sizes, perovskite films require less pressure for surface contact with the adjacent layer compared to big particle sizes.

Therefore, it is important to note that perovskite films with small particle size require low pressure, while those with big particle size require relatively higher pressure to achieve an optimum interfacial surface contact. Hence, an optimum pressure is needed for the adequate surface contacts to avoid the sink-in of particles into adjacent layers, which can damage the device.

To study the interfacial stress due to the applied pressure on the multilayered PeLED structures, Figs. 5(a)-5(f) present the results of finite element simulations of the device interface between the photoactive perovskite and electron transporting layers before and after pressure application. The results show that the interfacial surface contacts increased with increasing pressure between 0 MPa and 12 MPa.

There is an increase in the distribution of von Mises stress within layers and around the interfacial defects as the applied pressure increases. However, there is evidence of sink-in of the top layer to the bottom at higher pressure [Fig. 5(f)]. The PDMS anvil and top layers of the device deformed accordingly and curl round the particle as the surface contact improves. It is important to note that, by comparing the level of von Mises stress to the remotely applied pressures (which are in mega scale), the von Mises stresses in the layers are larger to induce crystallization.^{31–33}

B. Optical properties

The optical absorbance of the mixed halide perovskite $(CH_3NH_3PbI_{3-x}Cl_x)$ emitter is presented in Fig. 6(a). The results showed an increase in the absorbance of the emissive material with an increase in pressure from 0 MPa to 7 MPa within visible spectrum. As the amount of pressure approaches the optimum value, the absorption tends to reduce [Fig. 6(a), inset]. This increase in the absorbance can be attributed to increased crystallization and improved film quality. The results of the PL spectra are presented in Fig. 6(b). The increase in crystallization is evident in the PL results, as the peaks of the spectra shift slightly toward higher wavelengths with increasing applied pressure from 0 MPa to 7 MPa. The bandgaps that were estimated from the PL spectra are presented in Fig. 6(c) for films that were assisted with pressures between 0 MPa and 10 MPa. The bandgap reduces with increasing pressure from 0 MPa to 7 MPa. The reduction in the bandgap can be associated with increased crystallization of the perovskite films. However, the bandgap seems to increase when 10 MPa pressure is applied, which can be attributed to film damage. In PeLEDs, the low bandgap emitter implies lower energy for turn-on voltage, while the high bandgap emitter requires high energy for PeLEDs' turn-on. The bandgap energy is essentially used up during recombination of electrons and holes.

The XRD patterns of the perovskite emissive layer are presented in Figs. 6(d) and 6(e), while Fig. 6(f) shows the SEM image of the perovskite layers. Figure 6(f) shows that the films were uniformly spin-coated with nicely arranged grains. Figure 6(d) presents the dominant peak (110) that appeared at 21°, while Fig. 6(e) (inset) has the peak (220) at 42.8° for the as-prepared and all the pressureassisted films. The results show a significant increase in the (110) and (220) peaks for applied pressures between 0 MPa and 9 MPa. The increase in the peak intensity can be attributed to pressure-induced crystallization.

C. Pressure-effects on performance characteristics *1. Current-voltage curves*

The results of the current–voltage (I-V) characteristic curves of the fabricated PeLEDs are presented in Fig. 7(a). The I–V curves



FIG. 4. Effects of pressure on contact length (a) for different thicknesses of the perovskite films and (b) for different particle sizes or film roughness values.



FIG. 5. Computational modeling of interfacial surface contacts in perovskite light emitting devices, which shows the von Mises stresses within layers and interfaces: (a) before pressure application and [(b)–(d)] pressure-assisted devices at 1 MPa (b), 3 MPa (c), 5 MPa (d), 7 MPa, (e) and 10 MPa (f).



FIG. 6. (a) Effects of applied pressure on the absorbance of PeLED emitter (CH₃NH₃Pbl_{3-x}Cl_x): The inset show the increase in absorbance with very high applied pressures, (b) PL spectra of the perovskite emitter at different applied pressures, (c) effect of applied pressure on the bandgap of the emitter, (d) XRD patterns of the pressure-assisted perovskite film, (e) effects of applied pressure on the XRD peak intensity, showing the (110) peak and (220) peak (inset), respectively, (f) an SEM image of the perovskite film.



FIG. 7. Effects of pressure on the performance of PeLEDs: (a) current–voltage curves of complete PeLEDs at different applied pressures (0–10 MPa) and (b) turn-on voltage as a function of pressure.

show that there is a decrease in the turn-on voltage with increasing applied pressure [Fig. 7(b)]. It was observed that the turn-on voltage reduced from 2.5 V to 1.5 V for the pressures between 0 MPa and 7 MPa. These results can be attributed to improved interfacial surface contacts and crystallization of the films [Fig. 6(e)]. Similar results have been shown for multilayer structures of organic solar cells and organic light emitting devices.^{40,41} The increase in the interfacial surface contacts with applied pressure consequently decreases interfacial voids, which in turn enhances the work function alignment and charge transport. The increase in the transportation of charges increases recombination, which is evident in the reduction in the bandgap [Fig. 6(b)].

2. Mobility and defect density

The space charge limited conduction (SCLC) technique was used to provide insights into carrier mobility and defect trap density. The cross-sectional SEM images are presented in Figs. 8(a)-8(c) for hole-only devices that were assisted with pressures from 0 MPa to 10 MPa. The results show improved interfaces with an applied pressure of 7 MPa [Fig. 8(b)], while higher pressures result in the sink-in of layers [Fig. 8(c)]. To compare the defect density of the as-prepared and optimum pressure-assisted devices, the current density–voltage (J–V) curves of the single carrier devices were incorporated into the Mott–Gurney relation,⁵⁷ which relates the defect trap density



FIG. 8. [(a)–(c)] Cross-sectional SEM images of hole-only devices that were treated at different pressures, 0 MPa in (a), 7 MPa in (b), and 10 MPa in (c). (d) Effects of pressure on the trap filled voltage, trap density, and mobility for hole-only devices.

 (N_t) to the bias trap filled voltage (V_{TFL}) . This gives

$$V_{TFL} = \frac{2\varepsilon\varepsilon_o N_t}{qL^2},\tag{5}$$

where ε , ε_0 , q, and L are the relative permittivity of the perovskite layer, permittivity of free space, electronic charge, and thickness of the perovskite, respectively.

Figure 8(d) presents the J–V curves of the as-prepared and pressure-assisted (at 7 MPa) hole-only devices in a log-log scale. The result shows a decrease in the trap filled voltage from 0.28 V to 0.18 V for as-prepared and pressure-assisted devices, respectively. The trap density also decreased from 9.55×10^{16} cm⁻³ to 5.31×10^{16} cm⁻³, while the hole mobility increased from 41.1×10^{-6} cm²/Vs to 43.3×10^{-6} cm²/Vs.

V. SUMMARY AND CONCLUDING REMARKS

In this paper, a combination of analytical, computational, and experimental methods has been used to study the effects of pressure on the performance characteristics of perovskite light emitting devices. The salient conclusions arising from the work are presented below.

- 1. The application of pressure increases the interfacial surface contacts between adjacent layers in multilayered PeLED structures. The surface contacts are also shown to increase with reduced film thicknesses and particle sizes. The increased interfacial surface contact improves the work function alignment of layers, which enhances the transportation and recombination of generated holes and electrons.
- 2. The optical properties of the perovskite films increase with increasing applied pressure. The results show that the optical absorbance of the films increases with pressures between 0 MPa and 7 MPa. The increase in the absorbance of the perovskite film is associated with the reductions in the bandgap. The XRD patterns of the as-prepared and pressure-assisted perovskite films are compared. The results show a significant increase in the intensities of the (110) and (220) peaks with increasing applied pressure. This is due to an increase in crystallinity.
- 3. The decrease in the energy bandgap and crystallization at high pressure is evident in the device performance characteristics. The turn-on voltages of the PeLEDs were significantly reduced from 2.5 V to 1.5 V for applied pressures between 0 MPa and 7 MPa due to the reduction in the defect trap density. This reduction in the turn-on voltage is also attributed to the improvements in interfacial surface contacts within the multilayered structures of PeLEDs.

ACKNOWLEDGMENTS

The authors are grateful to the Pan African Materials Institute of the World Bank African Centers of Excellence Program (Grant No. P126974) and the Worcester Polytechnic Institute for financial support. The authors also appreciate Nelson Mandela Institution and the African University of Science and Technology (AUST) for their financial support.

DATA AVAILABILITY

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

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