



## Materials science communication

## Effect of lanthanum content and substrate strain on structural and electrical properties of lead lanthanum zirconate titanate thin films



Sheng Tong<sup>a,b,\*</sup>, Manoj Narayanan<sup>b</sup>, Beihai Ma<sup>b</sup>, Shanshan Liu<sup>b</sup>, Rachel E. Koritala<sup>c</sup>, Uthamalingam Balachandran<sup>b</sup>, Donglu Shi<sup>a</sup>

<sup>a</sup> College of Engineering and Applied Science, University of Cincinnati, Cincinnati, OH 45221, USA

<sup>b</sup> Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, USA

<sup>c</sup> Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

## H I G H L I G H T S

- PLZT thin films with different La dopant levels and thermal strains were fabricated.
- Heavier La doping decreased lattice parameter, grain size, and  $P_r$ .
- Compressive strain enhanced the values of  $T_c$ ,  $P_r$ , and  $E_c$  compared with tensile.
- Lattice parameters and grain sizes were smaller in thin films than in bulks.
- $P_r$ ,  $E_c$  were improved in thin films from those in bulks.

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## A B S T R A C T

We investigated the structural, electrical properties of  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  (PLZT) thin films under tensile (Pt/Si) and compressive ( $\text{LaNiO}_3/\text{Ni}$ ) strain-states, respectively. The lattice parameter, grain size, remanent polarization of the thin films decreased with increasing La content. For identical compositions, the Curie temperature, remanent polarization, and coercive field were always higher for films on  $\text{LaNiO}_3/\text{Ni}$  than Pt/Si. These suggest that the electrical properties of PLZT thin films can be tuned by altering the dopant level and substrate-induced strain levels.

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The lead lanthanum zirconate titanate,  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$  (PLZT,  $x/y/1-y$ ) was discovered in 1971 [1,2], and since that time, there has been considerable interest in the development of PLZT-film devices for various applications owing to their excellent ferroelectric and piezoelectric properties. One of the most attractive features of PLZT is that its behavior transitions from normal ferroelectric to relaxor with an increase in La content. Such phase transition can be easily recognized by the change in electrical behavior. For example, the temperature-dependent permittivity peaks would be sharp in normal ferroelectrics and diffuse in relaxors, and the shape of the polarization–electric field ( $P$ – $E$ )

loops would vary from square to slim [2]. The  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) compositions exhibit exceptional piezoelectric and ferroelectric properties around the morphotropic phase boundary (MPB) with Zr/Ti ratio of 52/48 because the monoclinic  $C_m$  phase enhances the possibility of polarization alignments [1,3]. The La donor dopants induce the distortion of unit cells for ease of domain switching and decrease the oxygen vacancies, leading to a higher relative permittivity ( $\epsilon_r$ ), spontaneous polarization ( $P_s$ ), and lower leakage current [4]. Hence, the PLZT ( $x/52/48$ ) compositions have been well investigated for their advanced dielectric and ferroelectric properties [3,5,6]. As a result of the substrate strain and size effects, the electrical properties and phase transitions of the ferroelectric thin films differ greatly from those of their bulk counterparts. We, therefore, studied the structural and electrical properties of  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  thin films with different La dopant concentrations on silicon and nickel substrates, and compared them to the bulk properties reported in the literature.

\* Corresponding author. College of Engineering and Applied Science, University of Cincinnati, Cincinnati, OH 45221, USA. Tel.: +1 630 252 6516; fax: +1 630 252 3604.

E-mail addresses: [shengt@mail.uc.edu](mailto:shengt@mail.uc.edu), [stong@anl.gov](mailto:stong@anl.gov) (S. Tong).

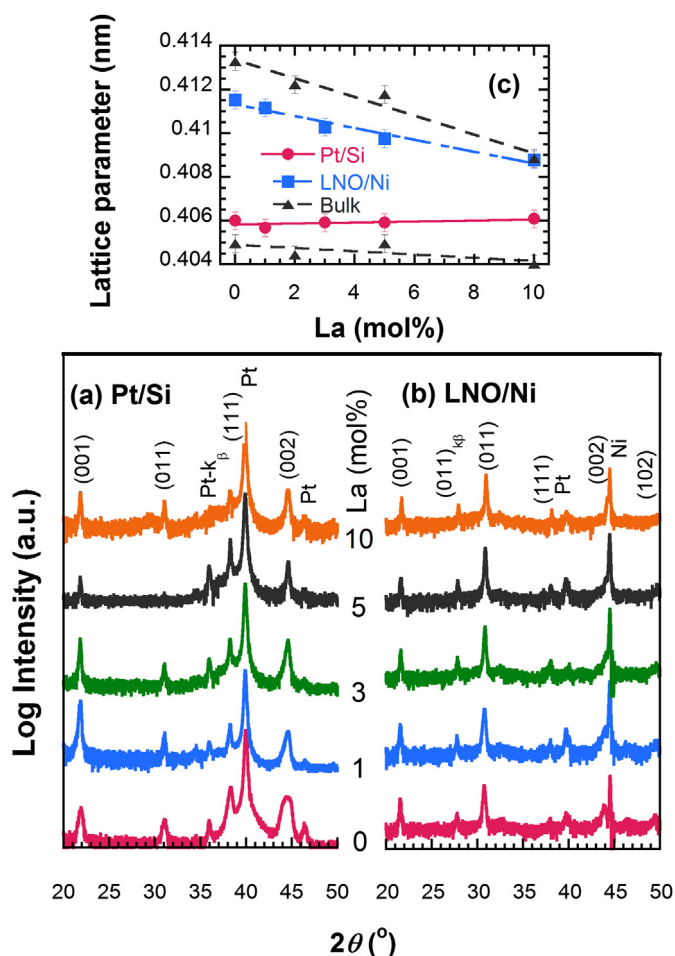
Using sol–gel chemistry based on acetic acid, we fabricated PLZT thin films ( $x/52/48$ , where  $x = 0, 1, 3, 5, 10$ ) on substrates of platinumized silicon (Pt/Si) and of nickel buffered with lanthanum nickel oxide (LaNiO<sub>3</sub> or LNO). The LNO buffer layer is included to avoid nickel oxidation and diffusion that forms a low-permittivity parasitic layer that contributes to series capacitance. Details on the solution preparation, deposition, and heat treatment conditions are reported elsewhere [7]. The thickness of the platinum bottom electrode on silicon substrate was  $\sim 500$  nm, and the final thickness of the LNO and PLZT thin films was  $\sim 400$  nm and  $\sim 500$  nm, respectively. Platinum top electrodes (250- $\mu$ m diameter and 100-nm thickness) were deposited through a shadow mask by electron-beam evaporation. The effects of donor dopants and substrates on thin film phases, morphology, dielectric properties and ferroelectric responses were studied by X-ray diffraction (XRD, Bruker AXS diffractometer), field-emission scanning electron microscopy (SEM, Hitachi S4700), LCR meter (Agilent E4980A) using an oscillator level of 0.1 V in conjunction with a Signatone QuieTemp probe station with hot stage (Lucas Signatone Corp., CA), and ferroelectric test system (Radiant Technologies PrecisionPremier II Tester) at 1 kHz, respectively.

The  $\theta$ – $2\theta$  symmetrical reflection XRD measurements were used to characterize the phases of the PLZT thin films. The XRD patterns in Fig. 1(a) and (b) indicate the formation of phase-pure perovskite with pseudo-cubic structure in all PLZT thin films fabricated on both substrates. In Fig. 1(c), the out-of-plane (planes normal to the

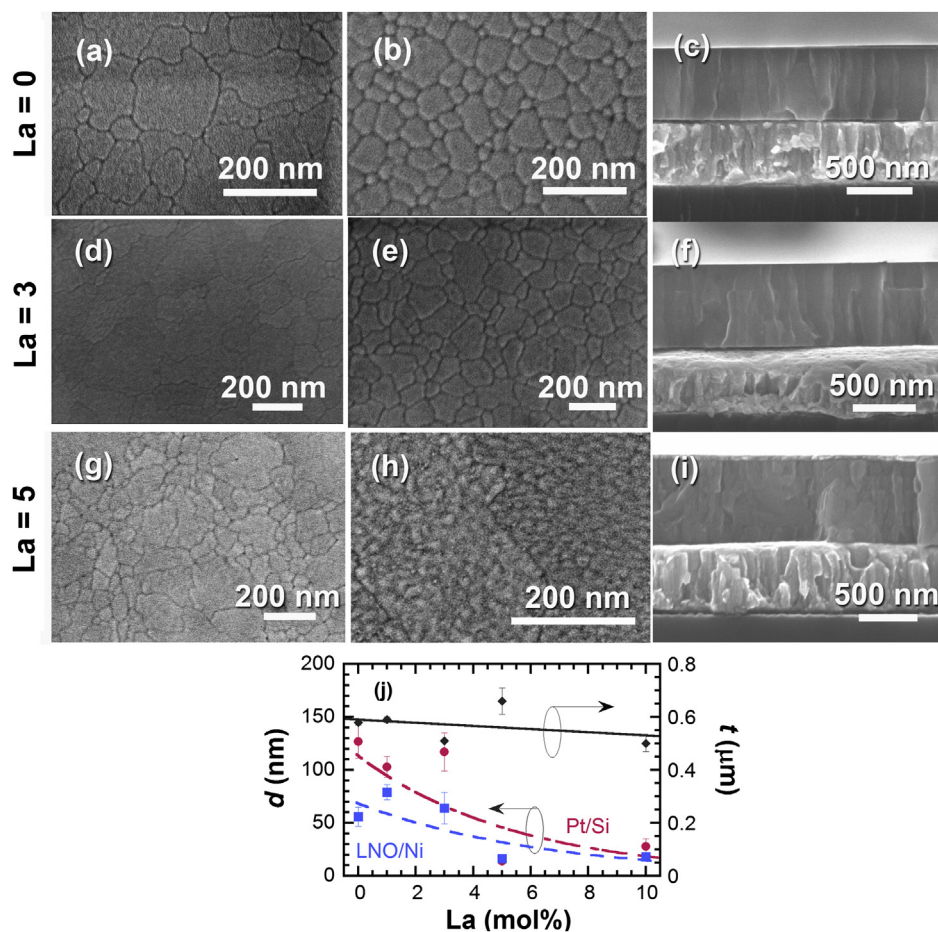
substrate surface) lattice parameters derived from (002) peaks decrease linearly with increasing La content in which slope of PLZT/LNO/Ni is much larger than that of PLZT/Pt/Si; this behavior is similar to values of  $c$  and  $a$  of bulk ceramic, respectively [3]. It can be explained by the nature of PLZT thin film strain states and domain structure. The thermal expansion coefficients of the thin film ( $\alpha_{\text{PLZT}} = 5.4 \times 10^{-6} \text{ K}^{-1}$ ) [8] and substrates ( $\alpha_{\text{Si}} = 2.6 \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha_{\text{Ni}} = 13.4 \times 10^{-6} \text{ K}^{-1}$ ) [9] indicate that the PLZT thin films deposited on silicon and nickel substrates are under tensile and compressive stress, respectively [10]. Thus, PLZT/LNO/Ni mainly demonstrates  $c$ -domains while  $a$ -domains dominate PLZT/Pt/Si [11,12]. A linear decrease in tetragonality ( $c/a$  ratio) of PLZT bulks with increasing La content shows a gradual transition from tetragonal to pseudo-cubic structure, due to the creation of A- and B-site vacancies and the reduction of oxygen vacancies [4]. Same tendency is expected in PLZT thin films, however, due to the 2–3 order differences in the grain sizes between thin films ( $<100$  nm) and bulk ceramic [4,13], the local tetragonality of the thin films cannot directly characterized. Nonetheless, it is reasonable to consider a higher tetragonality in PLZT/LNO/Ni compared with that of PLZT/Pt/Si based on the fact that the PLZT/LNO/Ni exhibits much larger out-of-plane lattice parameters as shown in Fig. 1(c). Note that the Pt (111) peak in Fig. 1 comes from the top electrode.

Planar SEM images of representative PLZT films doped with 0, 3, and 5 mol% La on both substrates are given in Fig. 2(a)–(f). The morphology of the films was smooth with dense and uniform grains without any obvious secondary phase (also confirmed by dielectric measurements below). The average surface grain sizes of the PLZT thin films deposited on the Si and Ni substrates were calculated and are shown in Fig. 2(j). Similar to bulk ceramic [14], the surface grain size of PLZT thin films decreased with the increase of La content in films formed on both substrates. However, the surface grain size of the PLZT thin films was 20–120 nm, which is 2–3 orders lower than that of bulk PLZT ceramic because of different crystallization temperature range [15]. The surface grain size of PLZT/Pt/Si is larger than that of PLZT/LNO/Ni at the same La dopant level. The cross-sectional SEM images of PLZT/Pt/Si shown as insets in Fig. 2(g)–(i) exhibit dense and columnar grains. No obvious secondary phases and defects were observed. As shown in Fig. 2(j), the measured thickness of the films is approximately 500 nm and is independent of the La concentration.

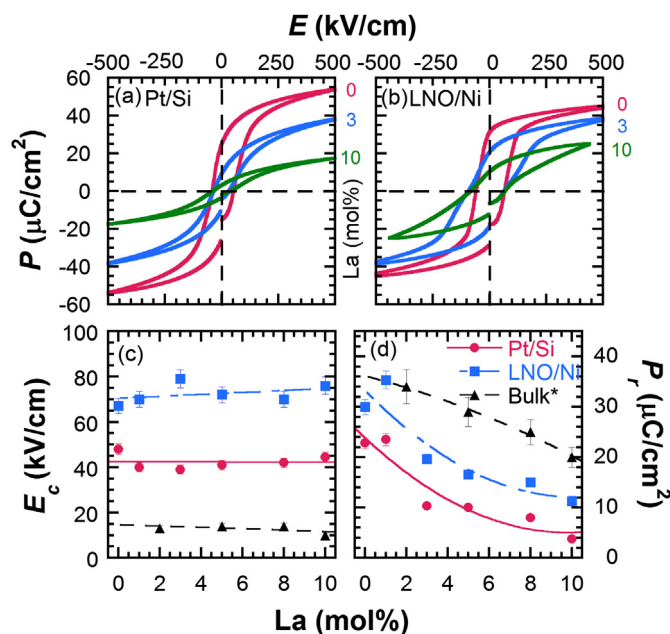
The dielectric and ferroelectric properties of PLZT thin films are strongly dependent on the La-dopant level, microstructure, and strain state (tensile or compressive). As shown in Fig. 3, with increasing La content from 0 to 10 mol%, the shape of the  $P$ – $E$  loops becomes slimmer and slanted for PLZT thin films on both Pt/Si and LNO/Ni. The remanent polarization ( $P_r$ ) and saturation polarization ( $P_{\text{sat}}$ ) also decrease dramatically in PLZT/Pt/Si and PLZT/LNO/Ni with increase in La content. The tetragonality decreases with increasing La content, leading to a reduction in spontaneous polarization in the unit cell. Therefore, the magnitude of the average net polarization in a domain/grain decreases, leading to a reduction in the measured macroscopic  $P_r$  and  $P_{\text{sat}}$  [14,16]. Although the measured  $P_r$  is correlated with the unit cell, this is not the case with the coercive electric field ( $E_c$ ). The macroscopically measured  $E_c$  is the “extrinsic” coercive field determined by domain nucleation, dynamic process, which is much lower than the “intrinsic” coercive field that is determined by the free energy profile of the B-site atom in the unit cell [17]. As can be observed in Fig. 3(c), the  $E_c$  values of PLZT bulk ceramic and thin films on Pt/Si and LNO/Ni are  $\sim 18$ ,  $\sim 40$ , and  $\sim 75 \text{ kV cm}^{-1}$ , respectively. The  $E_c$  is almost independent of La content (due to the extrinsic nature of the measured  $E_c$ ) for the thin film and bulk ceramic, whereas the  $E_c$  for thin films is 2–4 times higher than that reported for bulk ceramic [18,19]. The bulk  $E_c$  is lower than that of thin films because of grain size effects [16] and depolarization field at



**Fig. 1.** XRD patterns of PLZT thin films deposited on Pt/Si (a) and LNO/Ni (b) substrates. (c) Lattice parameters of PLZT thin films and bulk as function of La content (data for bulk ceramic from Ref. [3]).



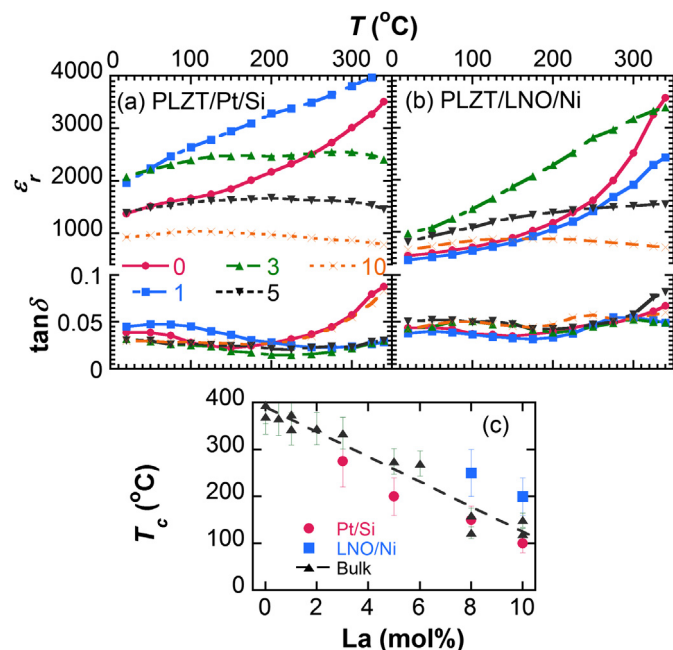
**Fig. 2.** SEM micrographs of PLZT (La content of 0, 3, and 5 mol%) thin films deposited on Pt/Si (planar: a, d, g; cross-sectional: c, f, i) and LNO/Ni (b, e, h). (j) Grain size  $d$  and thickness  $t$  as a function of La content.



**Fig. 3.** Hysteresis loops of PLZT (La = 0, 3, and 10 mol%) thin films deposited on Pt/Si (a) and LNO/Ni (b).  $E_c$  (c) and  $P_r$  (d) of PLZT as a function of La content for PLZT thin films and bulk ceramic. \*Ref. [3].

or the near electrodes which requires extra charge to compensate the polarization [20,21]. The  $P$ – $E$  loops of PLZT/LNO/Ni are “squarer” compared with PLZT/Pt/Si for the same La content. In other words, for an applied field the difference between the  $P_r$  and  $P_{\text{sat}}$  could be small. With an increase of La content from 0 to 10 mol%, the  $P_r$  values decrease from  $\sim 36$  to  $20 \mu\text{C}/\text{cm}^2$  for bulk ceramic,  $\sim 23$ – $4 \mu\text{C}/\text{cm}^2$  for thin films on Pt/Si, and  $\sim 30$ – $11 \mu\text{C}/\text{cm}^2$  for thin films on LNO/Ni. Although one would expect the  $P_r$  of stress-free bulk ceramics in Fig. 3(d) to fall between that of films under compressive and tensile stress, consideration has to be given to other major factors like grain size, dielectric thickness and depolarization field that plays an important role and influences the measured  $P_r$  of bulk ceramics compared to thin films [14,16,20,21]. The thermal strains induced by the thermal expansion mismatch between the substrate and thin film are critical in determining the domain morphology. The  $c$ -domain (polarization normal to the surface of the substrate) population and out-of-plane polarization ( $P_3$ ) decrease with increase in misfit strain from compressive to tensile [12,22,23], resulting in larger  $P_r$  in PLZT/LNO/Ni than that in PLZT/Pt/Si [as observed in Fig. 3(d)]. La ions soften the PLZT thin films from normal ferroelectrics into relaxors; however, the substrates partially retain the ferroelectric behavior, especially LNO/Ni substrates. The effect of compressive stress by nickel substrate on PLZT thin films can be compared to “hard” doping in PZT with  $\text{Fe}^{3+}$ , which limits the domain rotation and results in an increase in  $P_r$  and  $E_c$ , while the effect of the silicon substrate can be compared to “soft” doping with  $\text{Nb}^{5+}$  [24].





**Fig. 4.** Temperature-dependent dielectric properties of PLZT (La content of 0–10 mol%) thin films deposited on (a) Pt/Si and (b) LNO/Ni substrates at 10 kHz. (c)  $T_c$  of PLZT as a function of La content. The line is obtained by fitting the  $T_c$  data for PLZT bulk ceramic. The  $T_c$  values for PLZT bulk ceramic and PLZT (8/52/48) thin films were taken from Refs. [3,5,6] and Refs. [7,25], respectively.

The effect of La content and substrate on the temperature-dependent permittivity ( $\epsilon_r$  vs.  $T$ ) of PLZT thin films is shown in Fig. 4(a) and (b). The temperature corresponding to the permittivity maximum is considered as the Curie temperature ( $T_c$ ). In general, the room-temperature permittivity was higher for PLZT/Pt/Si compared with PLZT/LNO/Ni for all La concentrations; this substrate effect had been reported previously for PLZT with 8 mol% La [25,26]. In films on Pt/Si (LNO/Ni), the permittivity at room temperature increased from 1370 to 2070 (550–980) when La increased from 0 to 3 mol% and decreased to 920 (670) when the La content was further increased to 10 mol%. Similar to PLZT bulk ceramic [3,5,6], the permittivity response was flatter with diffuse phase transition peaks and lower  $T_c$  with increasing La content in thin films deposited on PLZT/Pt/Si and PLZT/LNO/Ni, in spite of the notable difference in the order of phase transition. Bulk ceramics follow first-order phase transition, whereas thin films follow second-order phase transition [18]. This difference is the reason for a sharp increase in the permittivity not being observed at  $T_c$  for thin films. The broadening of the  $\epsilon_r$ – $T$  curve is caused by factors inherent to the thin films: grain size [13,14], strain effect [27], and the “dead layer” effect [28]. The change in  $T_c$  with biaxial stress (compressive/tensile) induced by thermal expansion mismatch is given by the following equation [27,29]:

$$\Delta T_c = 4\epsilon_0 Q_{12} C \frac{Y}{1-\nu} \Delta\alpha \quad (1)$$

where  $\Delta T_c$  is the Curie temperature shift,  $\epsilon_0$  is the vacuum permittivity,  $Q_{12}$  is the electrostrictive coefficient,  $Y$  is the Young's modulus for PLZT,  $\nu$  is the Poisson ratio for PLZT, and  $\Delta\alpha$  is the thermal coefficient mismatch between substrate (Pt/Si or LNO/Ni) and PLZT thin film [10]. Since  $Q_{12}$  is always negative, we concluded that  $T_c$  will decrease in the case of tensile stress and vice versa for compressive stress. The change in  $T_c$  with increasing La content for

PLZT/Pt/Si and PLZT/LNO/Ni along with bulk ceramic is plotted in Fig. 4(c). As predicted by Eq. (1), the  $T_c$  for the films under compressive stress (LNO/Ni) is higher, whereas that for the films under tensile stress (Pt/Si) is lower compared with the bulk ceramic. Within the temperature range measured,  $T_c$  was observed for PLZT/LNO/Ni with La  $\geq$  8 mol% and PLZT/Pt/Si with La  $\geq$  3 mol%. Although the permittivity shows considerable difference with La content, as seen in Fig. 4(a) and (b), the dielectric loss was  $\sim$ 0.05 and did not vary much with increasing La content, temperature, or substrate.

In conclusion, we studied the effects of La content and substrate strain on the structural, ferroelectric, and dielectric properties of PLZT thin films. We found that the lattice parameters, grain sizes, and  $P_r$  of PLZT films decreased with increase in La content. The  $E_c$  was nearly independent of La content for films. For the same PLZT compositions, the grain size,  $E_c$  and room-temperature  $\epsilon_r$  of PLZT/Pt/Si were larger, and the  $P_r$  and  $T_c$  were lower than those of PLZT/LNO/Ni. These findings indicate that the PLZT electrical properties can be tuned by composition modification and substrate induced strain levels.

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