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Ferroelectric and dielectric properties of Li-doped ZnO thin films prepared by pulsed laser deposition

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ABSTRACT Zinc oxide is a very important piezoelectric material with lower preparation temperature, simpler structure and composition. By doping with some elements having smaller ionic radii, such as lithium, to substitute the zinc ions, it is expected that the center of the positive charge in a unit cell will not overlap with that of the negative charge in the same unit cell, leading to the appearance of the spontaneous polarization. Thin films of Li-doped ZnO with different compositions ($Zn_{1-x}Li_xO_y$, $x = 0.075$, 0.1, 0.125 and 0.15) have been prepared on heavily doped Si substrates by a pulsed laser deposition technique. In the films with $x = 0.1$ and $x = 0.125$, ferroelectric $P–E$ hysteresis loops were successfully observed. The remanent polarization and the coercive field of $Zn_{0.9}Li_{0.1}O_y$ and $Zn_{0.875}Li_{0.125}O_y$ were ($0.193\,\mu C/cm^2$, $4.8\,kV/cm$) and ($0.255\,\mu C/cm^2$, $4.89\,kV/cm$), respectively. An anomalous point in the dielectric spectrum of the Li-doped ZnO ceramics is observed, showing that the ferroelectric phase transition occurs around $67\,°C$ under 7.5 at. % Li-doped ZnO and $74\,°C$ under 10 at. %. If the remanent polarization of this material can be further increased, it may be used as a ferroelectric material.

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1 Introduction

Zinc oxide, ZnO, is a typical n-type piezoelectric semiconductor. It has a unique combination of piezoelectric, conductive and optical properties [1, 2]. Hence, it is being used increasingly in many devices such as ultrasonic transducers, surface-acoustic-wave (SAW) devices and chemical sensors. The crystal structure of zinc oxide is hexagonal ($P6_3mc$), which is suitable for fabrication of either a high-quality oriented or an epitaxial thin film [3]. Each Zn atom is tetrahedrally coordinated to four O atoms, such that the d electrons of the Zn atom hybridize with the p electrons of the O atoms. This compound is on the borderline between ionic and covalent semiconductors. Although stoichiometric ZnO is an insulator, it usually contains excess Zn atoms as a result of formation of large voids in crystals. Many physical properties,

such as electrical conductivity, piezoelectricity and defect structure, are greatly influenced by the amount of excess Zn and impurities [4]. First-principles studies of ZnO have been reported, focusing in particular on structural, electronic and piezoelectric properties [5–9]. Recently, ferroelectric activity was found in Li-doped ZnO [10], although no phase transition had been reported in pure ZnO at atmospheric pressure. Earlier, similar ferroelectric behavior was reported in a few other systems such as $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$ [11]. The ferroelectric nature is explained as follows: when the size of the dopant atom is smaller than the host atom that it replaces, it can occupy off-centered positions, forming electric dipoles locally, and thereby leading to ferroelectric behavior [12]. At low temperatures, it often happens that the off-centered ions become ordered and the crystal undergoes a ferroelectric phase transition [10]. In $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$, the ionic radii of the host (Pb, Cd) and dopant (Ge, Zn) atoms differ by 0.47 Å and 0.20 Å, respectively. It is believed that the large difference in ionic radii between the host Zn (0.74 Å) and the dopant Li (0.60 Å) is very important for the appearance of ferroelectricity in Li-doped ZnO [10]. Moreover, the electrical resistivity due to carriers can be improved by the introduction of Li ions [4], which is very useful when measuring dielectric properties. Here, the preparation of Li-doped ZnO thin films by the pulsed laser deposition (PLD) technique and the dielectric behavior as well as the ferroelectric properties of the Li-doped ZnO thin film will be reported.

2 Experimental details

The ceramic targets of $Zn_{1-x}Li_xO_y$, where $x = 0.075$, 0.1, 0.125 and 0.15, were synthesized by a solid reaction from starting materials ZnO (99.99%) and Li_2CO_3 (99.99%). The mixed powder, in a stoichiometric ratio, was ball-milled for 24 h and preheated at $700\,°C$. Pellets were formed at 500-MPa pressure and sintered at $1050\,°C$ for 3 h.

The PLD preparation of $Zn_{1-x}Li_xO_y$ films was carried out using a pulsed KrF excimer laser (LPX 205i, Lambda Physik) of 248-nm wavelength and 30-ns pulse width. The average energy was about 200 mJ per shot, and the pulse rate was 4 Hz. The films were deposited on a heavily doped Si substrate at $400\,°C$ for 1 h in flowing oxygen at a pressure of 30 Pa. The film thickness was about 400 nm. The Pt top electrodes with

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a dot size of 0.0314 mm^2 were deposited by the PLD method on Li-doped ZnO films. The structures of the Li-doped ZnO films were analyzed by a θ–2θ X-ray scan pattern using Cu K_α radiation. Atomic force microscopy (AFM) was used to examine the surface morphology of the films. Optical transmittance of the Li-doped ZnO films on a quartz glass substrate were analyzed by a Hitachi U-3410 spectrometer. Ferroelectric properties of the Li-doped ZnO films were measured with a RT66A tester.

3   Results and discussion

Figure 1 shows the X-ray θ–2θ scan pattern of $Zn_{1-x}Li_xO_y$ films deposited on Si substrates with $x = 0.075$, 0.1 and 0.15, respectively. All films obtained are well crystallized and show completely (001)-oriented growth. The lattice constants are $a = 3.244$ Å and $c = 5.199$ Å for the $Zn_{0.9}Li_{0.1}O_y$ films at room temperature. The reported values for pure ZnO films are $a = 3.249858$ Å and $c = 5.206619$ Å. The ratio a/c of $Zn_{0.9}Li_{0.1}O$ is 0.62397, which is slightly smaller than that of pure ZnO (0.62418). This value is related to the positional u parameter in the wurtzite structure by

$$u = \frac{a^2}{3c^2} + 0.25 \tag{1}$$

and the Zn–O bond length l is given by

$$l = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} . \tag{2}$$

The Zn–O bond lengths are 1.9745 Å for $Zn_{0.9}Li_{0.1}O$ and 1.9778 Å for pure ZnO [13]. In the analysis of our experiment, the X-ray-diffraction peaks have been magnified so that shifts in them can be studied (Fig. 1). It is found that the shifts are in the direction of increasing 2θ as the proportion of Li is increased. Using the Bragg theory, we can see that when 2θ becomes greater, d becomes smaller, which is consistent with the bond-length theory. Thus the lattice constant, d, decreased slightly with the increasing Li concentration. This small structural distortion may drive the ferroelectric phase transition.

The AFM studies of the surface morphology indicated that the films are reasonably smooth. The average roughness is about 10 nm for a scanning area of 2 μm × 2 μm (Fig. 2). The average grain size of the Li-doped ZnO films was about 100 nm.

Below room temperature, the dielectric constants of $Zn_{1-x}Li_xO_y$ ceramics with $x = 0.075$ and 0.1 do not vary; the same is true of the pure ZnO. But they show an anomaly corresponding to a phase transition at about 340 K. In $Zn_{1-x}Li_xO_y$ ceramics, both order–disorder characteristics (whether interaction is direct or phonon-mediated between off-centered Li ions) and displacive characteristics (relative translational shifts of Zn and O sublattices) are considered to play an important role in the phase transition. Above 400 K, dielectric constants increase gradually with increasing temperature. In Fig. 3, both the dielectric constants and the losses of the sample with $x = 0.075$ at frequencies of 100 Hz, 1 kHz, 10 kHz and 100 kHz are shown. The dielectric anomaly point (T_c) of $Zn_{0.925}Li_{0.075}O_y$ is at 341 K, and that of $Zn_{0.9}Li_{0.1}O_y$
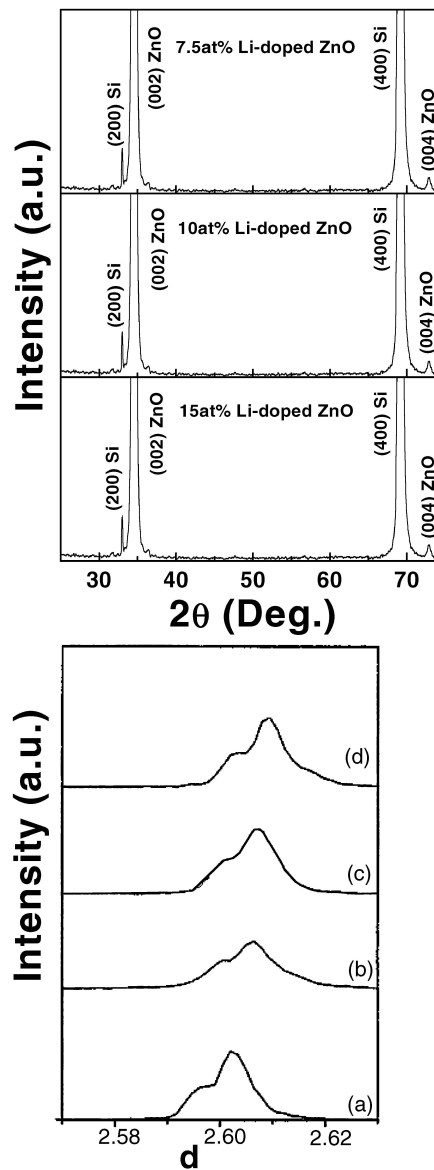
FIGURE 1   X-ray θ–2θ scan patterns of $Zn_{1-x}Li_xO_y$ films deposited on Si substrates with $x = 0.075$, 0.1 and 0.15. By the magnification of the (002) peaks of ZnO, **a** pure ZnO, **b** $Zn_{0.925}Li_{0.075}O_y$ films, **c** $Zn_{0.9}Li_{0.1}O_y$ films and **d** $Zn_{0.85}Li_{0.15}O_y$ films, it is seen that the peaks shift toward the direction where 2θ is greater as the doping increases

is at 347 K. T_c increases with increasing frequency. The same behavior was observed in $Cd_{1-x}Zn_xTe$. Terauchi suggested that such a material may have a glass-like nature [14], because the same phenomena are often observed in dipole glass systems. The dielectric loss at T_c (10 kHz) was only 0.0032. From Fig. 3, the dielectric losses showed a smooth increasing trend at all the frequencies. At high temperature the rate of increase of losses with temperature is greater than that at low temperature, due to an increasing contribution from electrical conductivity.

Figure 4a and b show the hysteresis loops of $Zn_{1-x}Li_xO_y$ films with $x = 0.1$ and 0.125, respectively. A positive remanent polarization ($+P_r$) of 0.193 μC/cm^2 and a positive coercive field ($+E_c$) of 4.8 kV/cm were recorded for the $Zn_{0.9}Li_{0.1}O_y$ film; those of the $Zn_{0.875}Li_{0.125}O_y$ film were 0.255 μC/cm^2 and 4.89 kV/cm, respectively. Com-
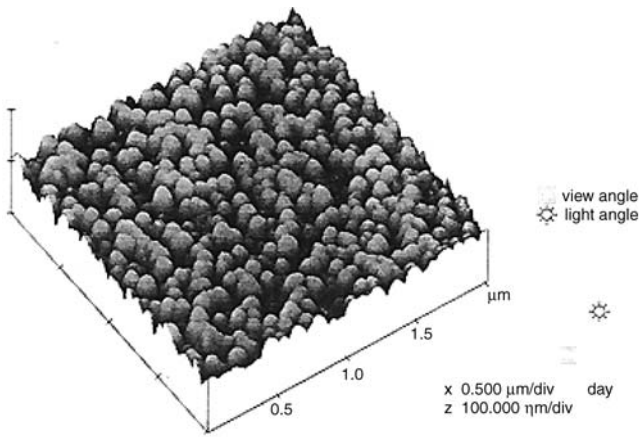
FIGURE 2   AFM image showing the surface morphology of the Li-doped ZnO films
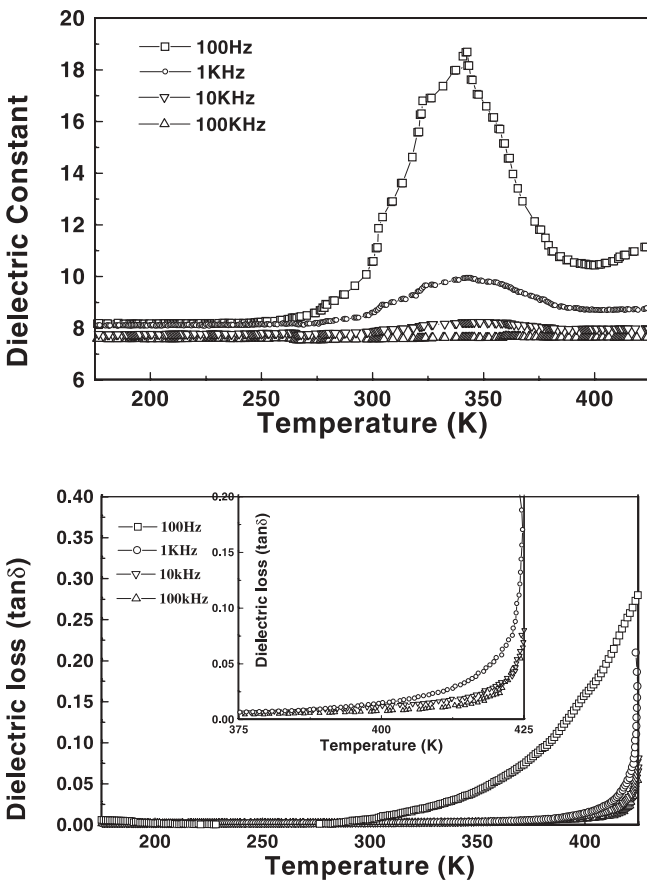

FIGURE 3   Dielectric constants of $Zn_{1-x}Li_xO_y$ ceramics with $x = 0.075$ at frequencies of 100 Hz, 1 kHz, 10 kHz and 100 kHz and their dielectric losses

FIGURE 4 P–E hysteresis loops of the ferroelectric $Zn_{1-x}Li_xO_y$ films: **a** $x = 0.1$ and **b** 0.125

FIGURE 5   Optical transmittance spectrum of the $Zn_{0.9}Li_{0.1}O_y$ films in the wavelength range 380–2000 nm

pared with Li-doped ZnO ceramics, the maximum nominal Li concentration of the films exhibiting ferroelectricity is higher. We think that this is due to volatility of lithium during deposition, causing the true lithium concentration in the films to be lower than the nominal lithium concentration.

Figure 5 shows the optical transmittance spectrum of $Zn_{0.9}Li_{0.1}O_y$ films. In the wavelength range 380–2000 nm, the transmittance curve was smooth and clearly oscillating. It shows that the surface of the films was very smooth and the
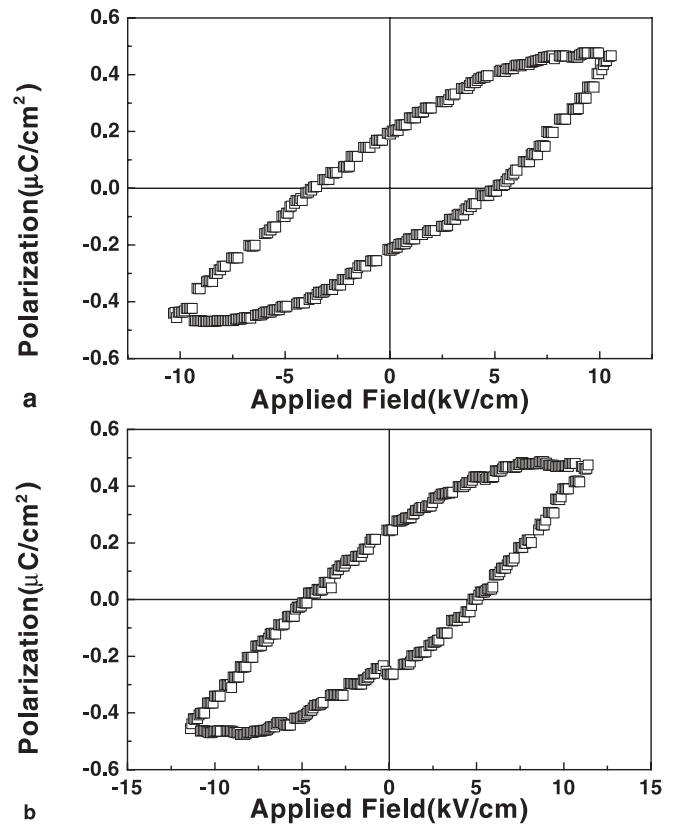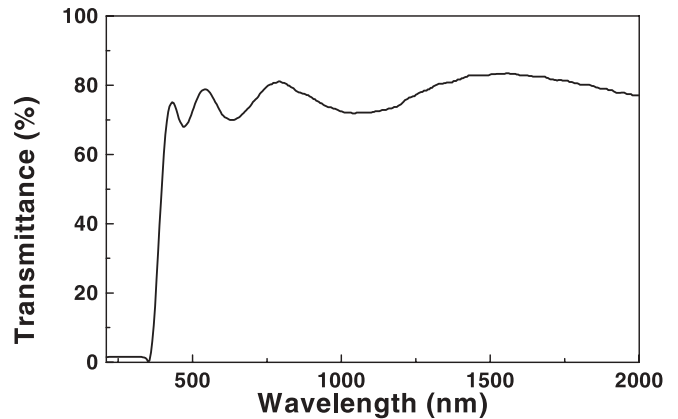
thickness was uniform. All the $Zn_{1-x}Li_xO_y$ films ($x = 0.075$, 0.1 and 0.15) prepared under the same conditions have the same absorbing edge of 380 nm (Fig. 6). The band gap of the film was calculated to be 3.25 eV. Thus the Li concentration has almost no effect on the band gap. We obtained a function $T_{max}(f)$ by connecting the maximum values of the transmittance spectrum (shown in Fig. 5) and a function $T_{min}(f)$ by connecting the minimum values. It is then supposed that $T_{max}(f)$ and $T_{min}(f)$ are continuous functions of the wavelength. Using the equation
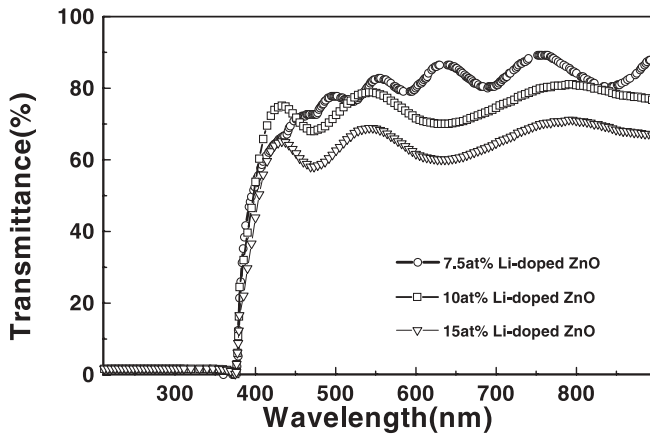
$$n = \sqrt{N + \sqrt{N^2 - n_0^2 n_1^2}}, \qquad (3)$$

FIGURE 6   Optical transmittance spectrum of the $Zn_{1-x}Li_xO_y$ films with $x = 0.075$, 0.1 and 0.15 in the wavelength range 210–895 nm

FIGURE 7   The refractive index versus wavelength curve of the $Zn_{0.9}Li_{0.1}O_y$ film, the pure bulk ZnO and a pure ZnO film

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} \, . \tag{4}$$

n_0 being the refractive index of the atmosphere ($n_0 = 1$), n_1 that of the substrate and n that of the film, we can calculate the value n as a function of wavelength. Compared with bulk ZnO and a pure ZnO film, the refractive index of the Li-doped ZnO is larger. It is the spontaneous polarization induced by Li doping in ZnO that causes this phenomenon, and this spontaneous polarization can switch, which makes the dielectric constant increasing. It is well known that the refractive index n is given by

$$n \equiv \frac{c}{v} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}} \, . \tag{5}$$

In terms of the relative permittivity K_e and the relative permeability K_m of the medium, n becomes

$$n = \sqrt{K_e K_m} \, . \tag{6}$$

The great majority of substances, with the exception of ferromagnetic materials, are only weakly magnetic; none is actually nonmagnetic. Setting $K_m = 1$ in the formula for n results in an expression known as Maxwell's relation [15],

$$n = \sqrt{K_e} = \sqrt{\frac{\varepsilon}{\varepsilon_0}} \, , \; [15] \tag{7}$$

ε_0 is a constant, so the refractive index increases with dielectric constant, which is why n is greater than that of the pure ones (Fig. 7). The thickness of the film can also be calculated from the equation

$$d = \frac{M \lambda_1 \lambda_2}{2 \left[n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1 \right]} \, , \tag{8}$$

where λ_1 is the wavelength of any one of the crests in Fig. 5 and λ_2 the wavelength of any one of the troughs (as long as the trough and peak chosen are not adjacent). $n(\lambda_1)$ and $n(\lambda_2)$ are the corresponding refractive indices. M is the number of the maxima and minima between λ_1 and λ_2.
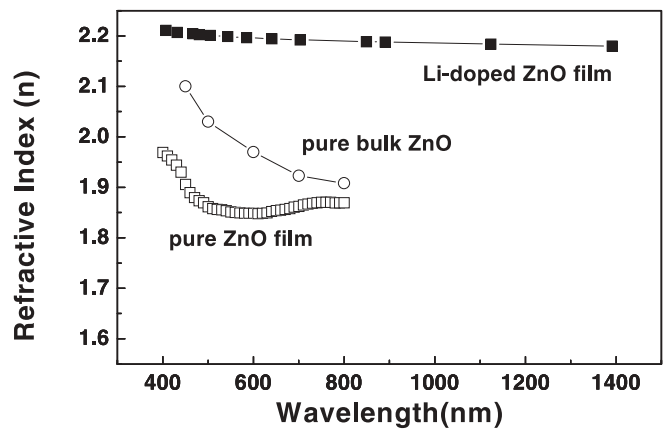
From (8), it is calculated that the film thickness is about 410 nm.

4   Summary and conclusions

     A dielectric system containing off-centered ions does not necessarily show ferroelectricity. It often becomes a dipole glass system such as in the case of Li-doped KCl [16]. On the other hand, $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$ undergo a ferroelectric phase transition. In our case of the Li-doped ZnO, there is a large difference in size between Zn and Li ions. It is expected that Li ions may occupy off-centered positions, replacing the host Zn ions and forming electric dipoles. This mechanism proposed by Katayama and Murase [17] explains the ferroelectric transition of Li-doped ZnO as well as those of $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$. Recently, first-principles studies have shown that differences in total energy of ZnO among the rocksalt, zincblende and wurtzite structures are quite small [5, 6]. In the tetrahedrally coordinated structures, these structural changes are closely related to the nature of bonding, whether it is ionic, mixed ionic–covalent or covalent. Though the mechanism of the phase transition is not clear at present, the effect of doping is closely related to the appearance of ferroelectricity. The structural modifications induced by Li dopant in ZnO may greatly affect the electronic and dielectric properties. With the appearance of ferroelectricity and ease of fabrication of high-quality thin films, ZnO is a promising candidate for a ferroelectric thin film in integrated ferroelectric devices.

     In summary, we have successfully grown completely (001)-oriented Li-doped ZnO films on a heavily doped Si substrate by PLD. Dielectric anomalies were found and the ferroelectric $P–E$ hysteresis loops were successfully observed at room temperature. It is believed that the replacement of host Zn ions by the smaller dopant Li ions is responsible for the appearance of ferroelectricity in the wurtzite-type ZnO piezoelectric semiconductor. However, the mechanism of the phase transition is not well understood yet. The effect of doping is closely related to the appearance of ferroelectricity. As thin films of ZnO have many applications, the observation of the ferroelectric nature in Li-doped ZnO films adds a dimension to the applications.

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