

## Low-temperature crystallized pyrochlore bismuth zinc niobate thin films by excimer laser annealing

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The crystallization temperature of  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  (BZN) films was reduced by a combination of conventional heating and irradiation with a pulsed KrF excimer laser. Both the energy density and substrate temperature affect the properties of laser-annealed BZN films. It was found that the crystallinity and dielectric properties improved after a postannealing at 400 °C for 2 h in an oxygen atmosphere. BZN films crystallized with an energy density of 27 mJ/cm<sup>2</sup> at a substrate temperature of 400 °C with postannealing showed dielectric properties comparable to those of rapid thermal annealed BZN films. Laser crystallization at substrate temperatures  $\leq 400$  °C makes integration with polymeric substrates possible. © 2005 American Institute of Physics.

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High-permittivity thin films are being investigated for applications in integrated high-density storage devices, decoupling capacitors, and electric-field tunable devices operating at high frequencies. For these applications, both high permittivity and low dielectric loss ( $\tan \delta$ ) are needed. However, paraelectric thin films, such as (Ba,Sr)TiO<sub>3</sub>, currently considered for these applications, are sensitive to temperature, and the properties are generally thickness dependent.<sup>1,2</sup> The family of bismuth zinc niobate (BZN) thin films have been demonstrated to have medium permittivity (170),<sup>3-6</sup> low loss (0.0005),<sup>5</sup> and a modest temperature coefficient of capacitance (TCC) (+150 to -400 ppm/°C) which can be tuned to near zero either by modulating the processing temperature or by making a phase mixture of the two end members of  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$  and  $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$ .<sup>3</sup> In addition, tunability as high as 55% has been observed for BZN films at room temperature.<sup>5</sup> These excellent dielectric properties make BZN an attractive material for tunable microwave device applications. BZN films have been successfully prepared by chemical solution deposition (CSD) and sputtering methods.<sup>3-6</sup> However, high-temperature annealing (>600 °C) is required to crystallize the amorphous films. This step leads to considerable constraints in combining the desirable characteristics of BZN films with those of thermally unstable substrates.<sup>7</sup>

One great advantage of laser annealing is that the laser radiation is strongly absorbed and produces high temperatures in a thin surface layer while the substrate remains at low temperature.<sup>8</sup> Laser annealing of ion-implanted or amorphous Si is well known.<sup>8,9</sup> Reports about laser crystallization of ceramic thin films, however, are very limited.<sup>10</sup> The possibility of a phase transformation from amorphous to x-ray crystalline has been demonstrated in  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.5+x}$  films.<sup>11</sup> Electrical data, however, are missing in many cases, probably because of damage induced by laser processing. In this work, a KrF excimer laser was used to assist in the crystallization of BZN films at low temperatures. The effects of energy density and substrate temperature on the crystal-

linity and dielectric properties were studied. In addition, postannealing in oxygen was also investigated.

Amorphous BZN thin films with a composition of  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  were prepared by a CSD method. The starting materials used were bismuth acetate, zinc acetate dihydrate (Aldrich Chemical Company, Inc., Milwaukee, WI), and niobium ethoxide (Chemat Technology, Inc., Northridge, CA). The solvents used were 2-methoxyethanol, pyridine, and glacial acetic acid (Aldrich). Details of the processing have been reported elsewhere.<sup>6</sup> BZN films were deposited by spincoating the precursor solution on Pt/Ti/SiO<sub>2</sub>/Si substrates (Nova Electronic Materials, Inc., TX). The as-deposited coatings were pyrolyzed for 1 min at 350 °C on a hotplate. This procedure was repeated until the desired thickness, typically 300 nm, was achieved. For laser crystallization, the sample was mounted onto a home-made heater using silver paste. The laser processing was carried out in ambient atmosphere with a pulse frequency of 10 Hz and an irradiation duration of 10 min. For electrical measurements, Au/Cr top electrodes with an area of  $1.3 \times 10^{-3}$  cm<sup>2</sup> were deposited by sputtering. The crystallinity of the films was characterized with a Scintag DMC-105 X-ray diffractometer using Cu K $\alpha$  radiation. The frequency dependent dielectric characteristics, tunability, and TCC were measured with a HP 4284A precision LCR meter. A Delta Design 2300 oven was used to control the temperature during the TCC measurements. Depth profiling of the optical properties was done using a rotating analyzer spectroscopic ellipsometer equipped with an achromatic compensator described elsewhere.<sup>12,13</sup> An incidence angle of 75° was utilized to measure model BZN films deposited on SrTiO<sub>3</sub> single-crystal substrates.

Figures 1(a)–1(c), respectively, show x-ray diffraction (XRD) patterns for the BZN films after different treatments: 400 °C annealing in oxygen for 2 h only, excimer laser treatment with an energy density of 27 mJ/cm<sup>2</sup> at a substrate temperature of 400 °C only, and excimer laser treatment with an energy density of 27 mJ/cm<sup>2</sup> at a substrate temperature of 400 °C plus 400 °C postannealing in oxygen for 2 h. No diffraction peak was observed in Fig. 1(a), indicating that 2 h oxygen annealing at 400 °C was not sufficient to crys-

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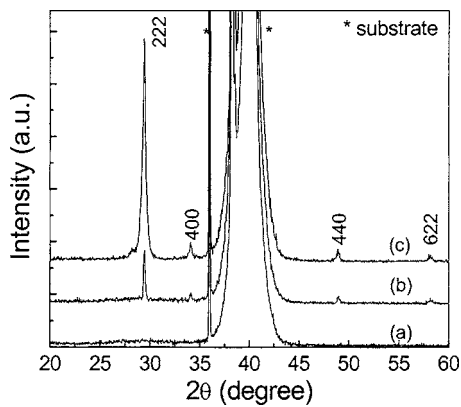


FIG. 1. XRD patterns for (a) BZN film annealed in oxygen at 400 °C for 2 h only, (b) BZN film treated with 27 mJ/cm<sup>2</sup> laser irradiation only, (c) BZN film treated with 27 mJ/cm<sup>2</sup> laser irradiation plus 400 °C postannealing in oxygen for 2 h.

tallize the amorphous BZN films. In contrast, diffraction peaks that match the BZN pyrochlore cubic phase were observed for the films annealed with a laser energy density of 27 mJ/cm<sup>2</sup> at a substrate temperature of 400 °C, indicating that the amorphous BZN film had been crystallized by laser irradiation. Further experiments revealed that both the substrate temperature and laser energy density affect the crystallinity of the laser annealed BZN films. At a substrate temperature of 400 °C, the laser irradiation did not crystallize the BZN film if the energy density was lower than 21 mJ/cm<sup>2</sup>. Above 27 mJ/cm<sup>2</sup>, the crystallinity was enhanced with increasing laser energy density. However, excessive laser energy induced a rough surface, degrading the BZN films. It also can be seen from Fig. 1 that the 400 °C oxygen postannealing greatly enhanced the crystallinity of the laser-treated BZN film, as the (222) diffraction peak was clearly strengthened.

The impact of laser annealing on BZN films was also examined using spectroscopic ellipsometry. For this, model samples on SrTiO<sub>3</sub> single crystals were prepared to avoid artifacts associated with changes in the optical properties of the Pt surface during heat treatment.<sup>13,14</sup> Samples were measured after pyrolysis, after laser annealing, and after a 400 °C oxygen anneal. The unknown optical properties of the film were described using a damped Sellmeier oscillator. Reference data were used for the optical properties of the SrTiO<sub>3</sub> single crystals.<sup>15</sup> The density depth profile was then

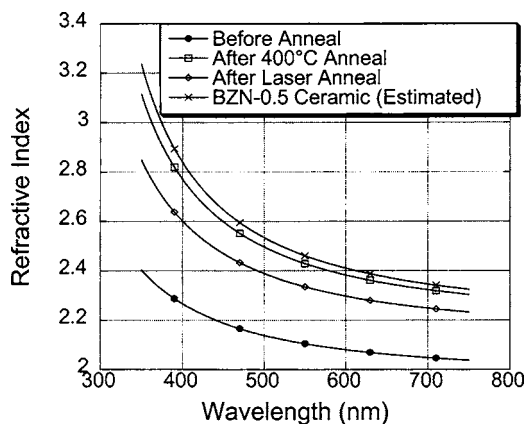


FIG. 2. Refractive index of the densest part of the BZN films at various points during the annealing process.

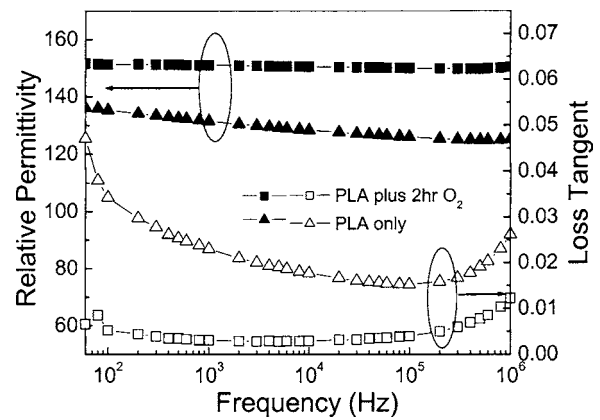


FIG. 3. Frequency dependence of relative permittivity and loss tangent of BZN films treated with 27 mJ/cm<sup>2</sup> at 400 °C only and with additional 2 h oxygen postannealing at 400 °C.

varied in the modeling until a good fit to the experimental data could be obtained.

It was found that the film undergoes a substantial thickness reduction (e.g., from 4426±86 Å to 3660±79 Å) during the laser annealing step. Simultaneously, the refractive index increased substantially, as shown in Fig. 2. This is consistent with the loss of organics from the film as well as the onset of crystallization. There is a second minor drop in thickness during the 400 °C oxidation step (to 3349±117 Å) tied to a further increase in the refractive index of the densest part of the film. The thickness change determined from the modeling of the ellipsometry data is consistent with independent profilometry measurements. Also shown in Fig. 2 is the refractive index of a hypothetical Bi<sub>1.5</sub>Zn<sub>0.5</sub>Nb<sub>1.5</sub>O<sub>6.5</sub> ceramic (bulk materials with this composition decompose during sintering). This curve was obtained starting from published data for Bi<sub>1.5</sub>Zn<sub>0.5</sub>Nb<sub>1.5</sub>O<sub>7</sub>.<sup>16</sup> The refractive index was then adjusted based on the differences in molecular weights and electronic polarizabilities of the two compounds.<sup>17</sup>

The comparatively low refractive index following laser annealing suggests that at that point the film is incompletely crystallized. The role of the oxygen anneal is then to complete crystallization, probably from the existing nuclei. Following this step, the refractive index of the densest part of the film is very close to that of the reference material, suggesting that near bulk properties have been achieved.

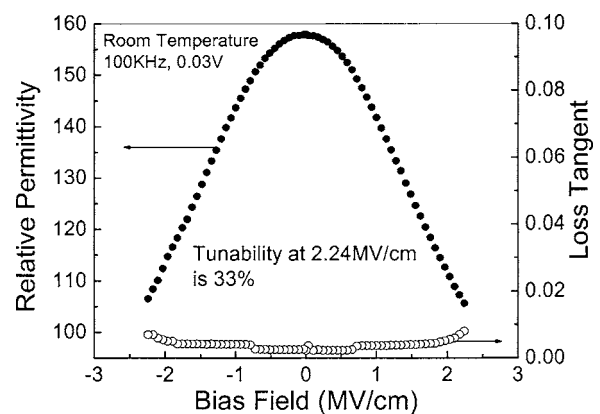


FIG. 4. Bias-field dependence of the relative permittivity and loss tangent of BZN films treated with 27 mJ/cm<sup>2</sup> plus 2 h oxygen post-annealing at 400 °C.

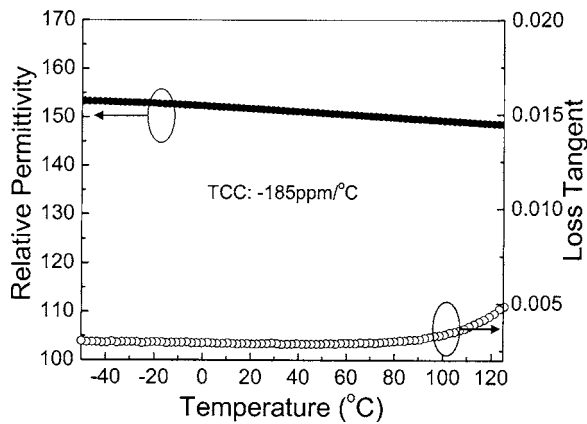


FIG. 5. Temperature dependence of the relative permittivity and loss tangent of BZN films treated with  $27 \text{ mJ/cm}^2$  plus 2 h oxygen postannealing at  $400^\circ\text{C}$ . Measurements were made at 100 kHz with an oscillation voltage of 30 mV.

The frequency dependences of the relative permittivity and loss tangent are shown in Fig. 3. For the sample treated with a laser energy density of  $27 \text{ mJ/cm}^2$  at a substrate temperature of  $400^\circ\text{C}$ , the relative permittivity and loss tangent value show some dispersion at low frequencies, consistent with space-charge polarizability. The dispersion in both relative permittivity and loss tangent values is reduced dramatically after a 2 h oxygen post-annealing, which could be due to a combination of reduction in the concentration of surface oxygen vacancies<sup>18,19</sup> by the oxygen postannealing and the improved crystallinity.

Figure 4 shows the room-temperature bias-field dependence of the permittivity and loss tangent at a measurement frequency of 100 kHz for the BZN films. The sample was crystallized with  $27 \text{ mJ/cm}^2$  at a substrate temperature of  $400^\circ\text{C}$  and annealed in oxygen for 2 h at  $400^\circ\text{C}$ . The loss tangent was below 0.2% at zero bias and remained below 0.8% up to a bias field of 2.24 MV/cm. The relative permittivity is 156 at zero bias, and decreased with increasing bias field. Defining the dielectric tunability with electric field as  $(\epsilon_{\text{max}} - \epsilon_{\text{min}}) / \epsilon_{\text{max}}$ , where  $\epsilon_{\text{max}}$  is the measured permittivity at zero bias, and  $\epsilon_{\text{min}}$  is the minimum measured permittivity at the maximum applied field, a tunability value of 33% was achieved at an applied field of 2.24 MV/cm, which is comparable with that of BZN films crystallized by rapid thermal annealing.<sup>6</sup>

The temperature dependence of the relative permittivity over  $-50$  to  $125^\circ\text{C}$  is shown in Fig. 5. The TCC, defined as  $(C' - C) / C$ , where  $C$  and  $C'$  are the capacitance at  $-50$  and  $125^\circ\text{C}$ , respectively, is  $-185 \text{ ppm}/^\circ\text{C}$ , which is slightly

smaller than the reported value of rapid thermal annealed (RTA) BZN films of this composition.<sup>6</sup> The resulting temperature stability of dielectric properties should be useful in designing temperature stable tunable components and is in marked contrast to the substantial temperature dependence observed in many paraelectric materials, such as  $(\text{Ba}, \text{Sr})\text{TiO}_3$ .<sup>1,2</sup>

In summary, a laser annealing process was developed for crystallizing CSD derived BZN films at substrate temperatures  $\leq 400^\circ\text{C}$ . The crystallinity and dielectric properties of the laser crystallized BZN films were greatly improved by a 2 h oxygen postannealing. Dielectric properties comparable to that of RTA crystallized BZN films at substrate temperatures  $> 600^\circ\text{C}$  were achieved. The low processing temperature for laser crystallized BZN films makes integration with polymeric substrates possible.

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