Picosecond Snapshot of the Speckles from Ferroelectric $BaTiO_3$ by Means of X-Ray Lasers

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A picosecond x-ray laser speckle has been conducted to study the dynamics of a disordered surface domain structure ($BaTiO_3$ with 90° c/a domains) as a function of temperature for the first time. The transient surface structures induced by ferroelectric domains decrease as temperature increases towards the Curie temperature T_c and completely disappear above T_c. The dramatic change of the spatial configuration of the c/a domains was observed to occur from a temperature 2 °C below T_c, near which the average correlated domain size at equilibrium decreases as $(T_c - T)^{0.37\pm0.02}$.

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Great concerns have grown about the speckles in the short-wavelength region with the advent of synchrotron radiation [1–4], since a shorter wavelength can bring a higher resolution to a disordered material. To the authors' knowledge, the accessible underlying dynamics from speckles has so far been limited in a form of slow temporal correlation in the x-ray region due to the small degeneracy parameter (i.e., the photon number contained in a coherent volume [5]) of the sources. The x-ray laser has an advantage, such as large degeneracy parameter, $\sim 10^8$, in the soft x-ray region compared to the other present x-ray sources [6,7]. Furthermore, the recent success of the operation of the x-ray laser in a transient collisional excitation (TCE) scheme has greatly shortened the x-ray pulse duration to an order of several picoseconds [8]. Such unique features of the TCE soft x-ray laser such as high brilliance, high coherence, and short pulse width bring out a new opportunity for the study of the instantaneous x-ray speckles diffracted from a disordered material, such as a ferroelectric material with random domain distribution.

For the ferroelectric material, the dynamics is still not clear how a stable macroscopic domain in the ferroelectric phase turns up from microscopic dipole fluctuations in the paraelectric phase. For example, the ferroelectric origin for $BaTiO_3$ still remains a question although it has been widely studied and applied. The clear soft phonon as observed in the other member, such as $PbTiO_3$ in the perovskites family, has not been observed in $BaTiO_3$ to date. The reason has been considered to be ascribable to the existence of the dipole clusters at or above the Curie temperature [9–11]. However, no other efficient methods can be used to observe directly their behavior due to the small size (down to nm) and the short lifetime (down to ps) for the cluster [12]. Therefore, an efficient extract of the transient status of the domain structure during the phase transition will help to understand this dynamic process, which is a matter of paramount importance not only from the theoretical point of view, but for practical applications as well.

Various methods have been employed to study the dynamic behavior of domains under applied field and with temperature. The techniques such as polarizing optical microscopy provide a relatively low resolution due to the long wavelength for visible light [13]. The scanning probe microscopy based techniques can provide a high spatial resolution for domain study [14–17]. However, they in principle belong to a long-time-averaged technique. Therefore, the transient status of domain structures is difficult to be extracted with them. X-ray scattering is a potential candidate for a dynamic study of phase transition; however, the transient domain structures seem still unable to be extracted with current synchrotron radiation due to its relatively long pulse (> 40 ps) and more severely due to its small degeneracy parameter (< 10) [18].

In this Letter, by means of the high brilliant soft x-ray laser, we report the first demonstration of the instantaneous measurement of speckles diffracted from a $BaTiO_3$ single crystal with multiple domain structure. The spatial correlations and the spatial power spectra of these domains were extracted from the speckle patterns. The transient surface structures induced by ferroelectric domains at various temperatures were successfully characterized for the first time, which yields a positive prospect for the further study of such an ultrafast fluctuating disordered system as the paraelectric state in $BaTiO_3$ near the Curie temperature, with a higher temporal and spatial resolution unattainable with other methods, by means of the picosecond x-ray laser speckles.

The experimental configuration is schematically shown in Fig. 1. The soft x-ray laser at 139 Å carrying about 10^{12}

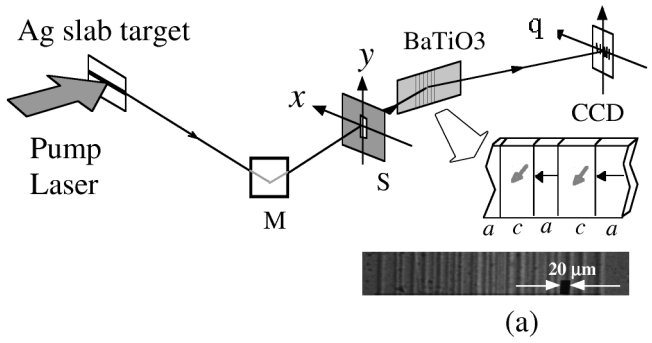

FIG. 1. Experiment setup. The TCE soft x-ray laser at 139 Å came from the Ag slab target pumped by a ~10 J, picosecond glass laser. The grazing angle was 10°. The coordinates, x and q, are in the horizontal direction. All the components were set in a vacuum ($\sim 10^{-5}$ Torr), where the temperature of the $BaTiO_3$ can be controlled from room temperature to 500 °C. The image in (a) is a photograph of the domains taken by an optical polarization microscopy at room temperature. M: Mo/Si multiplayer; slit: 80 μm (horizontal) × 200 μm (vertical).

photons within one pulse came from a silver slab target pumped by a 10 J, picosecond laser [8]. The average brilliance within one pulse is estimated to be about 10^{25} photons/(sec · mrad^2 · mm^2 · 0.01% bandwidth) for this soft x-ray laser. The pulse duration is estimated to be about 7 ps. The bandwidth, $\Delta\lambda/\lambda$, is typically around an order of 10^{-4} [19]. The equivalent incoherent disk diameter of the x-ray source, as described in an earlier Letter [20], was measured to be about 60 μm [21]. The degeneracy parameter, i.e., the number of the coherent photons, is estimated to be about 10^8 according to those measurements [8,21]. This value is much larger than that of the present synchrotron radiation.

In Fig. 1, a Mo/Si multilayer which has a high reflectivity for 139 Å at 45° incidence was used to produce a vertically polarized x-ray probing beam, since the Brewster angle $\theta_B = \tan^{-1}(n_1/n_2)$ is around 45° for this mirror. A 80 μm (horizontal) × 200 μm (vertical) slit located at 1.9 m from the silver slab target was used to produce a fully spatially coherent x-ray beam, because its aperture fell well within the transverse coherent region according to the measurement [21]. The sample used in the experiment was a flux-grown ferroelectrics $BaTiO_3$ single crystal with alternative a/c domains aligned in parallel. The Curie temperature was 122 °C. The sample was located close to the slit with its domain boundaries (walls) set in the vertical direction. The temperature of the sample was controlled from room temperature up to 130 °C with a precision of ±0.5 °C. The grazing angle was 10°. The diffracted speckle patterns were recorded by a soft x-ray charge-coupled device (CCD), 0.5 m far from the slit. The resolution of this system is estimated to be about 6 Å for the normal undulations of sample surface due to grazing incidence, and around 1 μm for the transverse domain size.

Figure 2(a) shows a pattern of the probing beam measured in a direction of free propagation of the x-ray beam via the slit. This pattern is a Fresnel diffraction pattern of the slit, where the horizontal profile was well fitted with a model of point source [22]. The photon flux was estimated to be 2×10^6 for a single x-ray shot from Fig. 2(a). The shot-by-shot fluctuations of the far field of the TCE soft x-ray laser did not affect the beam profile due to the extremely small acceptance angle of the slit. The setting error of the target position monitored by two CCD cameras might produce fluctuations for the beam horizontally. However, the beam fluctuations were estimated to be smaller than 4 μm at the sample and therefore contributed a negligible influence to the current speckle patterns compared to the horizontal dimension, 80 μm, of the slit.

Figures 2(b)–2(h) show a series of the speckles diffracted from a region of multiple a/c domains when heating the sample from 24 to 130 °C. Each pattern in Fig. 2 was taken with a single exposure of 7 ps by the TCE soft x-ray laser. Figure 2(b) is a typical pattern observed at room temperature 24 °C, where the pattern is clearly divided into two groups. As the temperature increased toward the Curie temperature, the speckle patterns apparently evolved into one group, as shown in Figs. 2(c)–2(g). Above the Curie temperature (T_c = 122 °C), the structures in the speckles disappeared and turned into

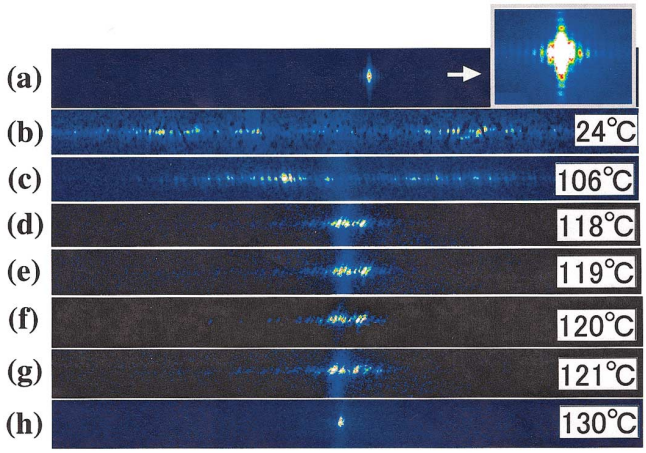

FIG. 2 (color). Speckle patterns measured by a single exposure of 7 ps with the TCE soft x-ray laser. (a) The direct probing beam pattern; (b) diffraction patterns via the a/c domain region at room temperature 24 °C; (c), (d), (e), (f), (g), and (h) correspond to the diffraction pattern from the same region of the sample at temperature 106 °C, 118 °C, 119 °C, 120 °C, 121 °C, and 130 °C, respectively. The Curie temperature of the sample is 122 °C. The scattering took place along the horizontal direction q, since the domain walls were set vertically. All these pictures are shown in a same scale for comparison.

one spot, as shown in Fig. 2(h), which was observed at 130 °C. The photon number for each of the patterns was estimated to be around the order of 10^5, indicating a reflectance of about 10% for the sample.

As shown in Figs. 2(b) and 2(c), the feature of the two obvious groups in each pattern for a relatively low temperature indicates a stable twin angle distribution along the c/a domain region. The speckles in each of the two groups originated mainly from the interference of x-ray photons scattered by the same type of domains (for instance, a domains), where the other type of domains (c domains) were invisible. The twin angles formed by adjacent c/a domains were estimated from the two central peaks in each pattern to be 0.47° and 0.3° for 24 °C and 106 °C, respectively, which are consistent with the result observed by atomic force microscopy [14,23].

Generally we can use a complex transmittance $\mathcal{T}(x) = \mathcal{T}_0(x)\exp[i\phi(x)]$ to describe domains projected on the slit, where the real part $\mathcal{T}_0(x)$ stands for the amplitude transmittance and the $\phi(x)$ for the phase retardation in the sample. The x is the horizontal coordinate along the x axis as shown in Fig. 1. We may define the matter correlation function as

$$\gamma(x) = \frac{\int_{-\infty}^{\infty} \mathcal{T}^*(x' + x)\mathcal{T}(x')dx'}{\int_{-\infty}^{\infty} \mathcal{T}^*(x')\mathcal{T}(x')dx'}. \quad (1)$$

On account of the random nature of the domain size, the matter correlation function $\gamma(x)$ can be readily extracted from the speckle pattern as $\gamma(x) = \mathcal{F}[I(q)]/\mathcal{F}[I_{\mathrm{Sp}}(q)]$, where the $\mathcal{F}$ is the operation of Fourier transform, the $I(q)$ is the domain-structure-diffracted intensity distribution along the q direction, and the $I_{\mathrm{Sp}}(q)$ is the specular reflection [22]. In practice, the specular reflection acting as a characteristic apparatus function of the system was obtained by measuring a diffraction pattern at a high temperature well above the Curie point. In characterization of the matter correlation function $\gamma(x)$, the diffracted intensity distribution measured with CCD was normalized by the total photons in each pattern to remove the influence of shot-by-shot intensity fluctuations of the TCE soft x-ray laser. The spatial power spectrum of the $\mathcal{T}(x)$, calculated from the Fourier transform of the matter correlation function $\gamma(x)$ according to Wiener-Khintchnie theorem [24], gives a statistic description of domain distribution in the wave number space.

Figures 3(a) and 3(b) show the power spectra at room temperature, which were extracted from the left-hand-side group and the right-hand-side group of the speckles shown in Fig. 2(b), respectively. The profiles in Figs. 3(a) and 3(b) are similar since they describe the same domain distribution, although a small discrepancy may be found due to the incomplete separation of the two groups. The interesting feature is that the maximum high-frequency oscillation is the same, which is 0.85 $\mu\mathrm{m}^{-1}$, corresponding to the average distance of 1.17 μm for the adjacent

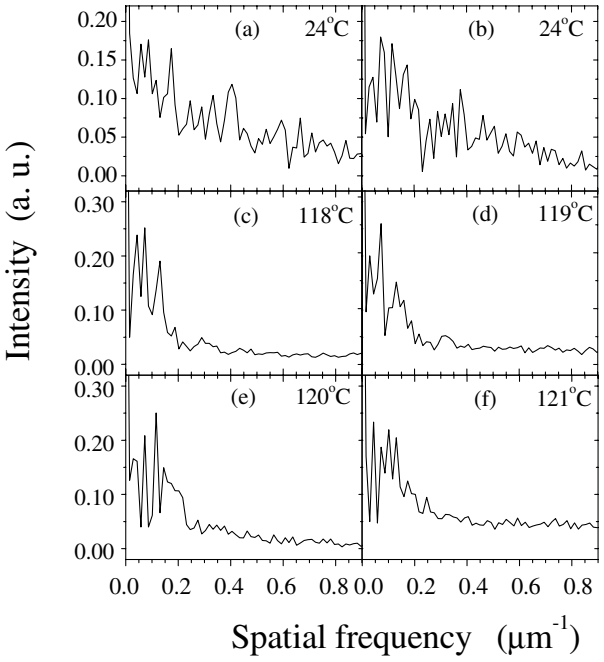

FIG. 3. The spatial power spectrum of the complex transmittance function projected on the slit. The spatial frequency is along the x direction shown in Fig. 1. (a) was calculated from the left-hand-side group and (b) was from the right-hand-side group of the speckles shown in Fig. 2(b); (c)–(f) were calculated from the speckles shown in Figs. 2(d)–2(g), respectively. The data shown in Fig. 2(h) were used as the apparatus function (specular reflection of the sample) in calculating the power spectrum from the speckles, as described in the text. The sharp peaks in these figures indicate a quasiperiodic distribution of the domains. The high-frequency oscillation has clearly been shown to evolve from 0.85 $\mu\mathrm{m}^{-1}$ for room temperature to 0.25 $\mu\mathrm{m}^{-1}$ for 121 °C, 1 °C lower than the Curie temperature.

two domains of the same type. Figures 3(c)–3(f) show the spatial power spectra, calculated from the data shown in Figs. 2(d)–2(g), respectively. The power spectra at 118 and 119 °C have the same profile, indicating the same surface status. The maximum oscillation frequency was shifted to 0.32 $\mu\mathrm{m}^{-1}$ in both Figs. 3(c) and 3(d), indicating that the domain size has turned larger due to the decrease of the twin angle, as observed by atomic force microscopy [12]. At 120 °C, the peak at 0.32 $\mu\mathrm{m}^{-1}$ has collapsed, and the power spectrum at the low-frequency part ranging from 0.05 to 0.22 $\mu\mathrm{m}^{-1}$ began to change as shown in Fig. 3(e). At 121 °C, this change becomes clearer as shown in Fig. 3(f). Above the Curie temperature, the speckles turned into a pure slit diffraction pattern, as shown in Fig. 2(h), indicating a complete annihilation of the a/c domain structures.

The correlation length σ_s, defined as the full width of the autocorrelation part of the matter correlation function $\gamma(x)$, is shown in Fig. 4 as a function of the reduced temperature $\mu = (T_c - T)/T_c$ near the Curie temperature. From the figure, one can clearly see that this average

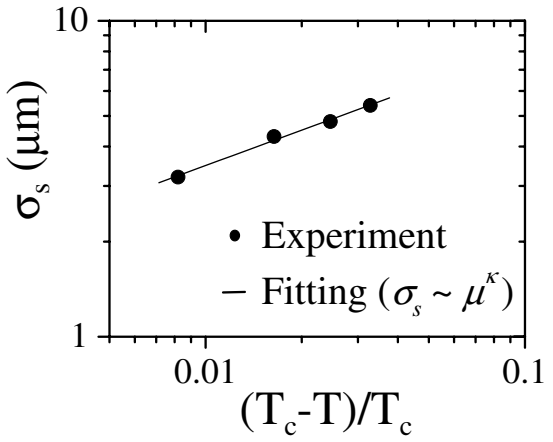

FIG. 4. The reduced temperature [$\mu = (T_c - T)/T_c$] dependence of the average correlated domain size σ_s at thermal equilibrium near the Curie temperature on a logarithmic scale. The solid line is the least-square fitting with $\sigma_s \propto \mu^{\kappa}$, which gives the exponent $\kappa = 0.37 \pm 0.02$.

domain size decreases in a form of the power law μ^{κ} as temperature approaches T_c. The exponent κ is determined to be 0.37 ± 0.02 by a least-squares fitting. The σ_s corresponds to the average correlated domain size. The power-law decrease of this correlated domain size near the Curie temperature implies the exsistence of the strong polarization fluctuations near the critical point.

In conclusion, a picosecond x-ray laser speckle has been successfully conducted to study the dynamics of a disordered surface domain structure via temperature for the first time. The combination of the high brilliance and the picosecond duration in the soft x-ray region shows that this is a powerful tool for studying the dynamics of an ultrafast fluctuating disordered system, such as a paraelectric state with a large amount of fluctuating clusters near the Curie point. By appropriate improvement of the x-ray intensity (such as focusing) and the spatial transverse resolution (such as 100 nm or smaller), the cluster-based speckles would be observable due to the birefringence of the domainlike clusters in $BaTiO_3$. This study is still in progress at present.

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