Generation of reflected second harmonic and phase transition in ferroelectric thin films

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Generation of the reflected second harmonic has been observed near the phase transition in ferroelectric thin films for the first time. A violation of fundamental polarization selection rules (a violation of the "*p, s* prohibition") has been observed for the second harmonic in media with a small-scale inhomogeneity.

Generation of the reflected second harmonic has found widespread use in recent years in research on the properties of surfaces,[1] interfaces,[2] and thin films.[3]

Generation of the reflected second harmonic obeys some selection rules of extremely broad applicability, which were observed in Ref. 4 and labeled "polarization prohibitions." These selection rules forbid the generation of an *s*-polarized, isotropic, reflected, second harmonic at smooth surfaces or in homogeneous thin films.

A violation of the polarization selection rules for second-harmonic generation at a rough surface of a semiconductor or a metal was observed in Ref. 5. The role played by an inhomogeneity of the medium in violating the polarization selection rules, on the other hand, has not yet been clarified. Ferroelectric thin films are a convenient material for such research, because of the inhomogeneity stemming from either their polycrystalline or polydomain structure.

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In this letter we are reporting a study of the generation of the reflected second harmonic in films with a zirconium–titanium–lead texture grown on the surfaces of silicon single crystals by the sol-gel method. The polycrystalline films had a thickness $d \sim 0.5$ μm and a typical crystallite size $\Delta \sim 300$–1000 Å. The films were pumped with p-polarized light from an Nd:YAG laser with a wavelength $\lambda = 1060$ nm. The film temperature was varied over the range $T \sim 300$–700 K, in which the films should exhibit a ferroelectric phase transition.

Figure 1a shows the temperature dependence of the intensity of the reflected second harmonic, $I_{2\omega}$. The initial stage of the heating, from 300 to 600 K, is accompa-

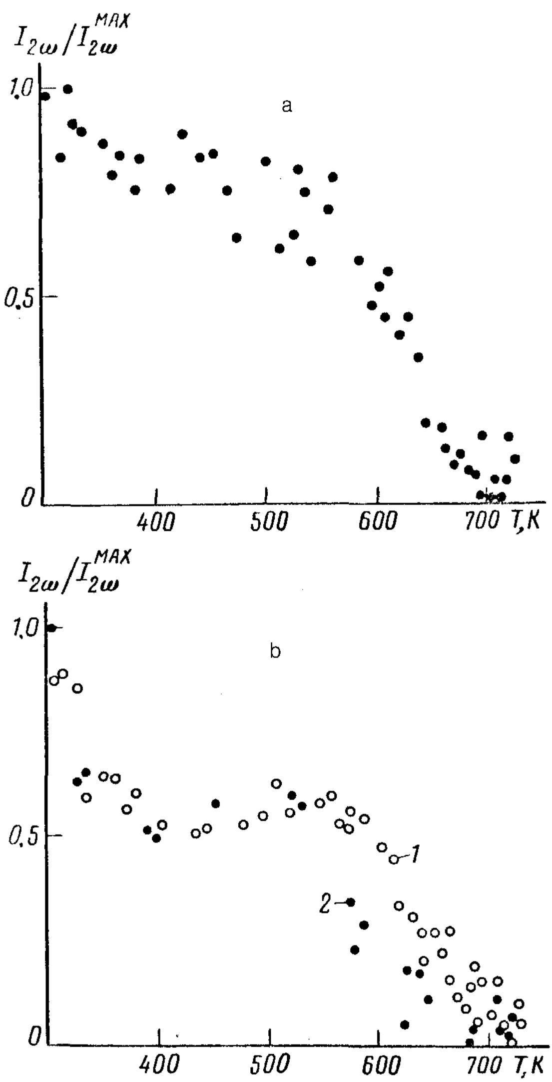

FIG. 1. Temperature dependence of the normalized intensity of the reflected second harmonic in the case of a p-polarized pump. a—For the overall second-harmonic signal; (b)—for the s-polarized component [1 (O)] and the p-polarized component [points 2 (●)] of the second harmonic.

nied by a slight decrease in $I_{2\omega}$, apparently a consequence of temperature-induced changes in the optical constants in the ferroelectric phase. Near $T \sim 620$ K, the second-harmonic intensity drops sharply because of the transition to the paraelectric phase. At $T \sim 650$ K, a plateau appears on the $I_{2\omega}(T)$ curve. On this plateau the intensity of the second harmonic is comparable to the signal from the surface of the substrate (silicon). The $I_{2\omega}(T)$ curve corresponds qualitatively to the temperature dependence of the spontaneous polarization, which is an order parameter in the transition to the polar phase. The corresponding temperature dependence for the s-polarized second harmonic, which is forbidden by the selection rules, is shown in Fig. 1b (points 1). Shown by points 2 in Fig. 1b is the corresponding behavior for the p-polarized second harmonic. The violation of the p, s prohibition and the high intensity observed for the forbidden second harmonic—this intensity is comparable to that of the allowed p harmonic—are consequences of the pronounced inhomogeneity of the films in both phases.

Analyzing the nonlinear response, we can partition the polycrystalline film into regions which have characteristic nonlinear-optics sources: the interior regions of crystallites and boundary layers 2δ thick (Fig. 2). The disruption of the symmetry of the medium due to the presence of the boundary surface is sensed over a distance $\lesssim \delta$ from the boundary. Consequently, the boundary layer has a nonzero second-order dipole susceptibility $\hat{\chi}^{(\beta,S)}$, where $\beta = (\Sigma,\Pi)$, in both phases. Here and below, Σ and Π mean the ferroelectric and paraelectric phases, and S and V specify the surface and the volume of a crystallite, respectively. In the ferroelectric phase, the lattice of a crystallite does not have an inversion center: The nonlinear response in the interior is de-

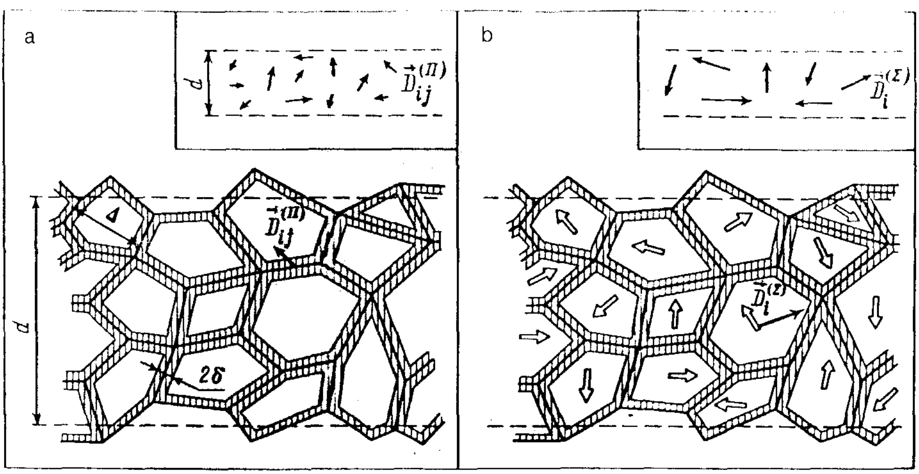

FIG. 2. Structure of the films in the (a) paraelectric and (b) ferroelectric phases. The light arrows show the directions of the ferroelectric axes in the microcrystallites. The hatched and unhatched regions correspond to regions with different nonlinear-optics responses. The insets show the equivalent systems of point dipoles which describe the nonlinear polarization of the film in the paraelectric and ferroelectric phases.

scribed by the dipole susceptibility $\hat{\chi}^{(\Sigma,V)}$. In the paraelectric phase, in contrast, the lattice has an inversion center, and the dipole susceptibility of the interior vanishes. The bulk response to the second-harmonic frequency appears in the next order of the multipole expansion and is described by the quadrupole susceptibility[1] $\hat{\chi}^{(\Pi,V)}$. In the ferroelectric phase, the ratio of the contributions of the interior and surface regions to the dipole moment of the crystallite induced at the frequency of the second harmonic is on the order of $\Delta/\delta \gg 1$, where Δ is a characteristic size of the crystallites ($\Delta \ll d$). In the paraelectric phase, the ratio of the bulk and surface contributions is on the order of $\Delta/d \ll 1$. Consequently, it is sufficient to consider only the bulk contribution in the ferroelectric phase and only the surface contribution in the paraelectric phases.

In the long-wavelength limit, the polarization of the film at the frequency of the second harmonic can be described by a set of point dipoles (since $\Delta \ll \lambda$) (see the insets in Fig. 2). In the ferroelectric phase, these are the dipole moments $D^{(\Sigma)}(2\omega)$ of the interior regions of the crystallites. For the dipole moment of crystallite i we have

$$\vec{D}_i^{(\Sigma)}(2\omega) = V_i \hat{\chi}_i^{(\Sigma,V)}(2\omega) : \vec{E}_i(\omega)\vec{E}_i(\omega), \tag{1}$$

where V_i is the volume of the crystallite, and $\vec{E}_i(\omega)$ is the local value of the pump electric field. In the paraelectric phase the dipole moments $\vec{D}^{(\Pi)}(2\omega)$, induced at the faces of the microcrystallites, play the role of the point dipoles. For the face separating crystallites i and j we have

$$\vec{D}_{ij}^{(\Pi)}(2\omega) = 2S_{ij}\delta\hat{\chi}_{ij}^{(\Pi,S)}(2\omega) : \vec{E}_i(\omega)\vec{E}_i(\omega), \tag{2}$$

where S_{ij} is the area of the face. The dipoles $\vec{D}^{(\beta)}(2\omega)$ are distributed with an average volume density $n^{(\beta)}$ in the film, where

$$n^{(\Sigma)} \sim 1/<V_i>,$$
$$n^{(\Pi)} \sim <N_i>/(2<V_i>) \sim (36\pi)^{1/3}/(2\Delta<S_{ij}>) \approx 3/(\Delta<S_{ij}>), \tag{3}$$

N_i is the number of faces of crystallite i, $\Delta \equiv \langle V_i \rangle^{1/3}$, and the angle brackets mean a statistical average over the various crystallites.

For a plane pump wave in a randomly inhomogeneous medium, the diffuse and depolarized components of the second harmonic arise from fluctuations of the nonlinear polarization. In the system under study here, fluctuations of this sort arise from the behavior of the components of the tensors $\hat{\chi}_i^{(\Sigma,V)}$ and $\hat{\chi}_{ij}^{(\Pi,S)}$. It is natural to suggest that we have $\langle \hat{\chi}_i^{(\Sigma,V)} \rangle = \langle \hat{\chi}_{ij}^{(\Pi,S)} \rangle = 0$ by virtue of the random orientations of the crystallites and their faces. The averaging of $\hat{\chi}_{ij}^{(\Pi,S)}$ is carried out over only the internal boundaries between crystallites. The reason is that, in examining the diffuse component of the second harmonic, we can ignore the regular contribution from the external faces, because of their low statistical weight in comparison with that of the large internal surface area of a film. We then find $\langle \vec{D}_i^{(\Sigma)}(2\omega) \rangle = \langle \vec{D}_{ij}^{(\Pi)}(2\omega) \rangle = 0$: The radiation generated by these dipoles is completely diffuse and depolarized. If $l_{\parallel,\perp}^{(\beta)} \ll \lambda$, where $l_{\parallel}^{(\beta)}$ and $l_{\perp}^{(\beta)}$ are correlation lengths characterizing the length scales of the fluctuations of $\vec{D}^{(\beta)}(2\omega)$ respectively in the plane of the film and in the direction normal to it (it is natural to assume that we have $l_{\parallel,\perp}^{(\beta)} \sim \Delta$) in this system, then the power of the diffuse second harmonic into a solid angle of 2π *sr* above the film is given by

$$W^{(\beta)}(2\omega) \sim l_{\perp}^{(\beta)}(l_{\parallel}^{(\beta)} n^{(\beta)})^2 < |\vec{D}^{(\beta)}(2\omega)|^2 >, \quad \beta = \Sigma, \Pi. \tag{4}$$

Using (1)–(3), along with the circumstance that we can use the estimate $\hat{\chi}^{(\Sigma,V)}$ and $\hat{\chi}^{(\Pi,S)}$ for the nonvanishing components of the tensors $|\chi^{(\Sigma,V)}| \sim |\chi^{(\Pi,S)}|$, we find an estimate of the ratio of the power levels of the diffuse second harmonic in the ferroelectric and paraelectric phases:

$$\gamma \equiv W^{(\Sigma)}(2\omega)/W^{(\Pi)}(2\omega) \sim 0.03 \frac{l_{\perp}^{(\Sigma)}(l_{\parallel}^{(\Sigma)}\Delta)^2}{l_{\perp}^{(\Pi)}(l_{\parallel}^{(\Pi)}\delta)^2}. \tag{5}$$

With $\gamma \sim 100$ (an experimental estimate) and $l_{\perp,\parallel}^{(\Sigma)} \sim l_{\perp,\parallel}^{(\Pi)}$, we find $\Delta/\delta \sim 50$. In other words, with $\delta = 10$ Å we find $\Delta \sim 500$ Å; this figure agrees qualitatively with the structural parameters of the system under study here.

In summary, we have observed generation of the reflected second harmonic near the phase transition in thin ferroelectric films for the first time. We have observed a violation of the *p*, *s* prohibition rules associated with fluctuations of the nonlinear susceptibility in highly inhomogeneous structures.

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