PHYSICAL REVIEW B VOLUME 62, NUMBER 1 1 JULY 2000-I

Laser-induced structural transitions in $YBa_2Cu_3O_y$ amorphous films with nanocrystalline clusters

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(Received 23 December 1999)

We investigated the influence of UV (KrF, $\hbar\omega = 5.01$ eV) pulsed laser irradiation on the atomic order and optical properties of amorphous YBaCuO films containing crystalline clusters of nanometer (up to 25 nm) size and characterized by high mobility of structural elements due to the lack of sharp interphase boundaries. The presence of crystalline clusters in amorphous medium leads to higher disorder of the latter, while electronic states in relatively narrow (≈ 2 eV) Cu $3d^{10}$ band become localized and practically do not participate in optical transitions. We found that UV radiation destroys the crystalline clusters, increases order in the amorphous medium and initializes the processes of $(11l)+(10l)\Rightarrow(00l)$ orientational transition. Increase of atomic order results in partial delocalization of electron states in the Cu $3d^{10}$ band and the conduction band switches over from Cu $4s^1$ to Cu $3d^{10}$.

I. INTRODUCTION

High-temperature superconductors (HTSC's) exhibit not only superconductivity, but also many other interesting effects, both at low and at high temperatures. This is true for ordered (crystalline and polycrystalline) and for disordered (amorphous) forms of HTSC's. In particular, YBaCuO thin epitaxial films in response to laser illumination are known to produce giant electric pulses, believed to be of thermoelectric origin.[1] Amorphous films of the same compound exhibit strong pyroelectric effect,[2] along with a high-temperature coefficient of resistance.[2,3] These properties of amorphous YBaCuO films form the basis of their proposed application as uncooled infrared detectors.[2,4]

Interest in the interaction of optical radiation with HTSC's has also a more fundamental character and is to a large extent stimulated by the nature of charge carriers in these materials. HTSC's appear to be metals, but in many respects they behave as highly degenerate semiconductors with metallic conductivity. Transition from insulating to superconducting behavior in the process of oxygen doping is one of the most characteristic features observed in these compounds.

Earlier research has shown that illumination of HTSC samples allows not only to investigate the electron states in various ranges of energy[5–10] but also to modify dynamically their properties. Generation of nonequilibrium charge carriers in this manner (''photodoping'') increases conductivity and enhances superconductivity in metallic samples. In insulating samples, it can even lead to dielectric-metal transition and transform an insulator into a superconductor.[11–14]

Photogeneration of charge carriers and nonequilibrium superconductivity are not the only effects of laser irradiation. Under short-wave (blue and green) medium power irradiation we observed irreversible and stable photocoloring of our amorphous YBaCuO samples. The hue imprinted in this manner matched the color of the laser used for the irradiation.[15] We found also that the irradiation tends to induce phase transitions in systems, which are in strongly nonequilibrium conditions. Disordered systems, characterized by high mobility of various structural elements appear to be especially prone to such transformations.

In this paper we report on the influence of laser irradiation on atomic order and optical properties of amorphous YBaCuO films containing nanosize crystalline clusters. To be more explicit, the characteristic property of the films used in the experiments is the presence of microscopic crystalline (≈ 200 Å) and mesoscopic semicrystalline (≈ 20 Å) fluctuations of atomic order in the disordered continuum. The clusters are either dielectric, with atoms ordered in the system of $(11l)$ planes, or metallic, represented by the family of $(00l)$ planes.[3] The presence of these clusters appears to be crucial for understanding the physical behavior of the films.

By utilizing the laser energy and its composite interactions with the sample (photogeneration of bound excitons in the optical transitions O $2p \Rightarrow$ Cu $3d^{10}$ and generation of a heat pulse) we expected to stimulate phase transitions $(11l)\Rightarrow(00l)$, similar to those observed earlier in the plasma created during pulsed laser deposition of YBaCuO films,[3] and to develop a system of $(00l)$ metallic clusters in the amorphous medium. Another premise is that the generation of bound excitons during charge transfer transitions O $2p \Rightarrow$ Cu $3d^{10}$ should play an important role in structural changes, since the coupling energy of exciton formation contributes to the coupling energy between copper and oxygen atoms. No diffusion over considerable distances is involved and structural transformations can be caused by moving the atoms over distances comparable to interatomic ones.

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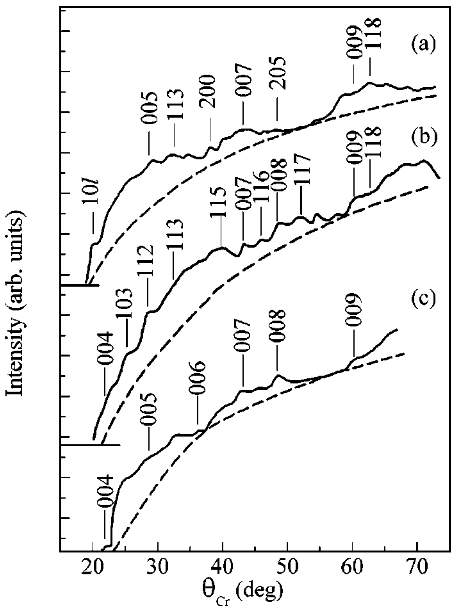

FIG. 1. Diffraction patterns of the investigated samples: initial (a), after two laser pulses (b), and after five laser pulses (c). Dashed lines represent the incoherent background.

II. EXPERIMENTAL RESULTS

The investigated amorphous YBaCuO films were deposited on glass substrates at room temperature and at 270 mTorr oxygen pressure by laser ablation from *123* stoichiometric target. We used KrF excimer laser ($\hbar\omega = 5.01$ eV) with pulse duration 25 ns and energy density of 1.5 J/cm^2 at the target surface. The samples were then irradiated in ambient atmosphere at 1 s intervals by 2 or 5 light pulses of the same laser at energy density of 0.1 J/cm^2, i.e., 3–4 times below the ablation threshold of YBaCuO,[16] although rather close to the YBaCuO vaporization threshold.[17]

Atomic structure of the samples was determined from x-ray diffraction patterns of $\mathrm{Cr}\,K_\alpha$ radiation. In order to detect atomic clusters with different degrees of order, particular attention was paid to the fine structure in the distribution of the diffusive intensity of coherent and incoherent x-ray scattering. Optical transmission spectra were investigated at room temperature and in quantum energy interval $\hbar\omega = 0.5 - 4.5$ eV.

The observed diffraction patterns were always exhibiting three characteristic regions of x-ray scattering (see Fig. 1, in which typical patterns recorded for the investigated samples are shown): (i) diffusive maximum (halo), the result of coherent scattering on small (~ 20 Å) crystalline-like clusters; (ii) incoherent background from scattering on the disordered medium between clusters; (iii) intensity fluctuations in the form of small peaks on the halo, the result of scattering on coarse (> 100 Å) crystalline clusters with lowered dimensionality.

From the diffraction patterns one can determine the integral intensities I_{coh} and I_{incoh} of coherent and incoherent scattering, respectively, as well as average cluster size by measuring the half-width and angular position of the diffraction maxima.[3] In a similar manner integral intensities of scattering on crystalline clusters I_c and on amorphous clusters I_a can be determined. We found that laser irradiation generally leads to the reduction of the intensity of coherent x-ray diffraction, this being caused by the reduction of crystalline cluster number and size (from 230–240 Å to 150–170 Å). By contrast, the incoherent diffraction component attains maximal value for five-pulse irradiation.

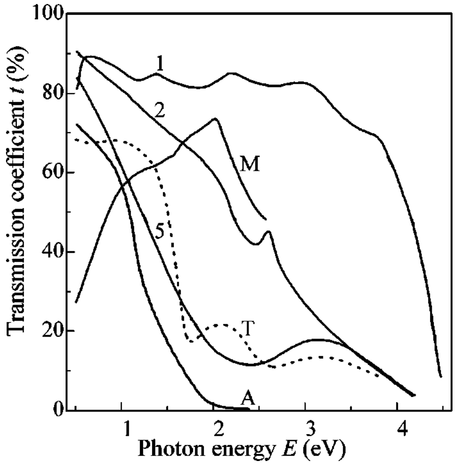

FIG. 2. Optical transmission spectra of YBaCuO films. (1) Initial nonirradiated amorphous sample, (2) after irradiation by two laser pulses, (5) after five laser pulses, (*M*) orthorombic film with $T_c = 91$ K, (*A*) amorphous film deposited by cathode sputtering, (*T*) crystalline film with tetragonal structure.

Further analysis of the intensity of fluctuation maxima indicates qualitative changes in atomic order induced by the laser irradiation. This is observed by the increase of volume fraction of clusters with dominant atomic order in the form of $(00l)$ plane fragments at the expense of clusters with different ordering $(10l)$ and $(11l)$. After irradiation more than 90% crystalline clusters are composed of $(00l)$ plane fragments. In this sense we can talk about the structural transition $(10l) + (11l) \Rightarrow (00l)$ induced by the irradiation. Let us remind the reader that charge transport in HTSC's is along $(00l)$ planes, while the material with atoms ordered in a system of $(11l)$ planes exhibits dielectric properties.[18]

We measured also the coefficient of optical transmission t defined as

$$t = I/I_0 = f(R)\exp[-\alpha(\omega)d], \tag{1}$$

where I and I_0 denote the intensity of incident and transmitted radiation, respectively, $\alpha(\omega)$ is the coefficient of optical absorption, d is the sample thickness, and $f(R)$ is some function of reflection coefficient R; in the simplest case $f(R) = 1 - R$.

The results of optical transmission spectra measurements are plotted in Fig. 2. The fine structure seen in the long-wave and medium-wave spectrum regions of the nonirradiated sample is due to the presence of crystalline clusters.[3] The spectrum of an amorphous YBaCuO film obtained by cathode sputtering (plot *A* in Fig. 2), which does not contain such clusters,[26] has a completely different character and is shifted approximately for 3 eV towards the longwave region. For comparison purposes, we show also in Fig. 2 the transmission spectrum of a film with tetragonal structure (plot *T*), as well as that of an orthorombic film with $T_c = 91$ K (plot *M*). Laser irradiation of amorphous films causes significant decrease of their transparency in the whole range of photon energies $\hbar\omega$ and considerably changes the spectrum shape. In the long-wave part of the spectrum, there appears an extended region in which the transmission coefficient decreases nearly linearly with increasing photon energy. In the middle part of the spectrum (at $\hbar\omega = 2.56$ eV for two laser pulses and at $\hbar\omega = 3.1$ eV for five laser pulses) is formed a maximum, initially rather narrow and then broadening at higher laser energy, preceded by a minimum at a nearly constant position (2.38 and 2.44 eV).

Film temperature during irradiation was measured in a rather primitive bolometer setup (the sample was deposited on a thin copper strip acting as a bolometer). We recorded a surprisingly low mean surface temperature $T_s = 620\,°\mathrm{C}$ after $\tau_d \sim 1$ μs following the pulse incidence. This measurement is inconclusive in the sense that nothing can be said about the maximal temperature immediately after pulse incidence, as the detection circuit had insufficient time resolution (τ_d was apparently set by the thermal time constant of the bolometer). Nonetheless, the measured T_s value can be safely assumed as the lower limit of the surface temperature. The upper limit, following the analysis of Otsubo *et al.*[17] can be taken as the melting temperature of (crystalline) YBaCuO ($T_s \cong 1100\,°\mathrm{C}$). This conclusion has been confirmed by our own experiments with superconducting YBaCuO films, which have sustained irradiation by a few tens of the same laser pulses without losing their superconductive properties, i.e., thermal damage done to them was not extensive. A simple fit to the experimental data shows also that the temperature drops rapidly to less than half of its surface value at the film-substrate interface.

Atomic force microscope (AFM) images recorded in the so-called ‘‘tapping’’ mode and shown in Fig. 3 constitute direct evidence that the high-temperature front has been passing across the film surface, causing a phase transition from amorphous to more ordered glassy state accompanied by glass softening. The striking differences between surface morphology of the untreated sample shown in Fig. 3(a) and the samples irradiated by two [Fig. 3(b)] and five [Fig. 3(c)] pulses cannot be explained in any other way.

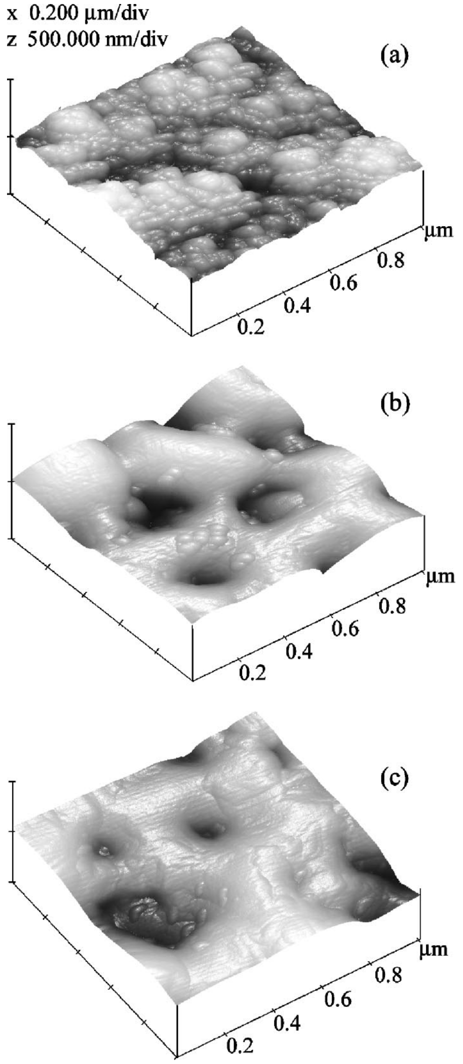

FIG. 3. Atomic force microscope images of amorphous YBaCuO film (a) initial (nonirradiated); (b) irradiated by two laser pulses; (c) irradiated by five laser pulses.

III. STRUCTURAL TRANSITIONS AND DENSITY OF STATES

The experimental data suggest that the principal source of the laser-induced spectral changes, including the formation of linear segments, is the augmentation of the volume occupied by the crystalline $(00l)$ clusters with metallic conductivity. The presence of these clusters leads to the build-up of strong intrinsic electric fields and leads to the appearance of Urbach ‘‘tails’’ in optical absorption. This effect is in many aspects analogous to the Franz-Keldysh effect,[19,20] but involves internal and not external electric fields. In such a case the spectral dependence of optical absorption coefficient α at frequencies below the threshold can be expressed as[21]

$$\alpha(\omega) = \alpha(\omega_t)\exp[-\hbar(\omega_t - \omega)/\Delta_0], \tag{2}$$

where $\hbar\omega_t$ is the threshold energy and Δ_0 denotes a characteristic energy independent of frequency. From Eqs. (1) and (2) we can obtain after simple manipulations

$$\frac{\partial t}{\partial(\hbar\omega)} = \frac{-f(R)d\hbar\alpha(\omega_t)}{\Delta_0}\exp[-\alpha(\omega)d] \times \exp[-\hbar(\omega_t - \omega)/\Delta_0], \tag{3}$$

or the normalized derivative of transmissivity with respect to photon energy

$$\frac{1}{t}\,\frac{\partial t}{\partial(\hbar\omega)} = \frac{\alpha(\omega)d}{\Delta_0}. \tag{4}$$

Equation (4) can be applied to determine experimentally the quantity Δ_0. Especially useful are the linear parts of the spectrum $t(\hbar\omega)$, where the derivative $\partial t/\partial(\hbar\omega)$ is independent of ω in a relatively broad range. The values of Δ_0, calculated in this manner, are given in Table I. In the same table we present the numerical values of quantities B and C defined from the linear approximation $exp(x) \approx 1 + x$, valid for small x, as applied to Eqs. (1) and (2):

TABLE I. Calculated optical properties of the irradiated samples.

No. of pulses	Δ_0 eV	C	B cm^{-1}	$\alpha(\hbar\omega_t)$ eV	$\hbar\omega_t$ eV	$\hbar\omega_c$ eV
2	0.520	1.21	0.248	2.58 10^3	1.368	4.87
5	0.817	1.37	0.649	1.06 10^4	1.387	2.11

$$t \approx f(R)[C - B\hbar\omega], \tag{5}$$

$$\alpha(\omega) \approx \alpha(\omega_t)[1 - \hbar(\omega_t - \omega)/\Delta_0]. \tag{6}$$

Hence

$$B = \alpha(\omega_t)d/\Delta_0, \tag{7}$$

$$C = \alpha(\omega_t)d[1 + \hbar\omega_t/\Delta_0]. \tag{8}$$

In Table I, we also introduced ω_c from $t(\omega_c) = 0$, or

$$\omega_c = C/B = \Delta_0 + \hbar\omega_t. \tag{9}$$

For the validity of the above analysis the most important question is whether the threshold energy $\hbar\omega_t$ indeed can be used to characterize the spectrum. Fortunately, as seen from Table I, the $\hbar\omega_t$ value is practically identical (within 2%) for both irradiated samples, notwithstanding the considerable differences in their transmission spectra, and this value is close to the charge transfer gap (CTG) $E_{\mathrm{CT}} \approx 1.37$ eV for $\mathrm{YBa_2Cu_3O}_y$.[10]

The intensity of optical transitions across CTG in the nonirradiated sample is low, and these transitions are related to the presence of crystalline clusters. The optical absorption edge is shifted into the range $\hbar\omega > 4$ eV, i.e., not only higher than its position for the insulator state but also higher than for the metallic state (cf. plot *M* in Fig. 2). Taking into account that the optical width of the forbidden gap in amorphous YBaCuO films without crystalline inclusions is about 1.5 eV (Ref. 26) (cf. plot *A* in Fig. 2) it is evident that in the nonirradiated sample, optical transitions across the CTG, from the valence band into the conduction band O $2p \Rightarrow$ Cu $3d$, are strongly suppressed.

The nature of this effect can be explained by taking into account the triple band model of density of states in HTSC, the elements of which were introduced in Refs. 22–24. According to this model, in our material, the band of hole states in the metallic clusters is located between two Hubbard bands (see Fig. 4). CTG in the dielectric state is constituted by the gap $\mathrm{E_{CT}}$ between the filled valence band O $2p$ and the empty upper Hubbard band Cu $3d^{10}$ [Fig. 4(c)]. Extended tails in the distribution of the density of states are due to the fact that the dielectric state is represented mainly by the amorphous medium between clusters.

The Cu $4s^1$ band usually does not participate in the charge transfer. The role of the conduction band in YBaCuO is played by the upper Hubbard band Cu $3d^{10}$. However, this band is narrow ($\cong 2$ eV) and, according to Anderson,[25] amorphisation of YBaCuO fills it completely with localized states. This process is aided by the presence of crystalline clusters, which introduce considerable stresses and broken bonds into the medium. Disorder in the distribution of atoms means that for the Cu $3d^{10}$ band the Anderson localization criterium is fulfilled, which for *d* states has the form[25] $V_0 \geqslant B$, where V_0 is the random potential and B is the band width. Probability of optical transitions involving localized states is very low.[25] Such transitions are hardly present in the nonirradiated films, in which the role of the conduction band is indeed played by the Cu $4s^1$ band and the Cu $3d^{10}$ band is transformed into a band of localized states between the valence and conduction bands.

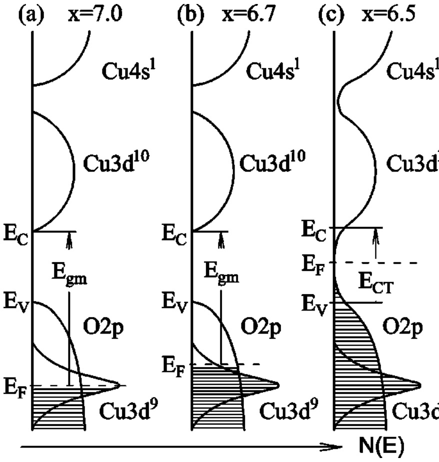

FIG. 4. Density of state models of $\mathrm{YBa_2CuO}_x$ for $x = 7.0, 6.7, 6.5$. E_F denotes Fermi level, E_V: valence band, E_C: conduction band, and E_{gm} is the distance between Fermi level and the bottom of conduction band in the case of metallic conductivity.

The effect of laser irradiation is the increased order in the amorphous matrix and, as a consequence, delocalization of Cu $3d^{10}$ states and increased probability of their participation in optical transitions across CTG. In fact, laser treatment results in the switching of conduction bands Cu $4s^1 \Rightarrow$ Cu $3d^{10}$. An important role in this respect is played by the fracturing of crystalline clusters and reduction of their size. The reduction of cluster size is also accompanied by the reduction of broken bonds density.

According to the band diagram shown schematically in Fig. 5, tunneling effects enabled in the presence of metallic clusters and the associated random electric fields lower the threshold photon energy for interband optical transitions.

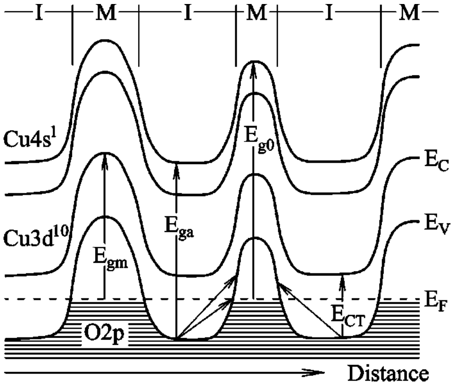

FIG. 5. Band diagram of an amorphous film containing crystalline clusters with metallic conductivity. E_{ga} is the distance between Fermi level and the effective conduction band Cu $4s^1$ in the amorphous matrix, and E_{g0} is the same distance in the metallic cluster.

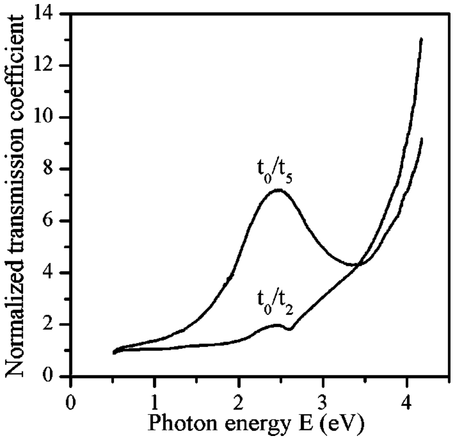

FIG. 6. Normalized optical transmissivity after irradiation by two and five laser pulses.

This explains the experimentally found linear dependence of transmissivity on photon energy (Fig. 2), especially pronounced in laser irradiated samples. As shown in Fig. 5, if the Fermi level in the amorphous region is located in the middle of the CTG, then the minimal photon energy needed for charge transfer transitions is just about half of CTG, in good agreement with the data shown in Fig. 2.

In Fig. 6 we show the normalized transmission spectra $t_0(\omega)/t_2(\omega)$ and $t_0(\omega)/t_5(\omega)$, where t_x denotes the sample transmissivity after irradiation by x laser pulses. Since t_0 remains nearly constant in a broad range of photon energies $\hbar\omega$, the plotted quantities reflect the density of states in the relevant bands. Thus the broad maximum at 2.4 eV apparently is related to the maximum of the density of Cu $3d^{10}$ states. Minimum at 3.3–3.4 eV corresponds to the region between Cu $3d^{10}$ and Cu $4s^1$ states, while the sharp rise at $\hbar\omega>3.5$ eV is due to optical transitions between the valence band and the Cu $4s^1$ band.

IV. CONCLUSIONS

The observed effects in laser irradiated amorphous films (structural transitions and the resulting optical phenomena) cannot be explained by a single cause. Several basic mechanisms must be considered. First of all let us discuss the role of heat dissipated in the sample by the incident laser pulse and the resultant temperature rise. Assuming that this rise does not reach the melting temperature (at least not in more than a few top atomic layers), the main effect of heat dissipation would be generation of thermal stresses and temperature gradients. The latter may generate substantial electric fields.[1,2] One cannot also exclude higher local temperature arising in the crystalline clusters, which exhibit higher optical absorption.

Structural transformations are aided not only by thermal effects but also by all electron mechanisms related to the generation of electron-hole pairs. The rate at which these pairs are created in our experimental conditions exceeds 2×10^{29} cm^{-3} s^{-1}. With lifetimes of the order of 10^{-10} s the resulting nonequilibrium concentration $\Delta n>2\times10^{19}$ cm^{-3} is capable of providing instantaneous metallic conductivity of the amorphous medium for the duration of the laser pulse. Such screening by nonequilibrium charge carriers weakens the chemical bonding between the atoms and favors structural changes.

The general trend of the structural changes can be also stimulated by the excitons generated in the optical transitions O $2p\Rightarrow$ Cu $3d$. Due to the high laser photon energy (5.01 eV), the generation of bound excitons capable of changing the bonding energy of oxygen and copper atoms can occur only within metallic clusters, as the maximal energy allowed for optical charge transfer transitions in the insulator is much lower (3.0–3.5 eV). In this manner the growth of $(00l)$ clusters is favored.

Another possible mechanism to be considered is the interaction with strong electric fields created by the laser illumination. The appearance of such fields is caused by the photogeneration of electron-hole pairs, whose concentration exponentially decreases with distance from the film surface. Lifetime of majority (hole) carriers is several orders of magnitude longer than the lifetime of minority (electron) carriers,[12] or the recombination rate of electrons (involving localized states in CTG) is much higher than the hole recombination rate. Consequently, the pulsed generation of electron-hole pairs is accompanied by an exponential distribution of positive charges and an appearance of electric field pulses, whose intensity in our case exceeds 10^5 V/cm. Ionic component in the chemical bonds of HTSC materials is very important and the influence of electric field on the processes of atomic ordering in amorphous samples can be very effective.[27] The important point is that the directions of the electric field and the temperature gradient coincide. The proposed mechanism is an alternative to the purely thermoelectric one discussed in Refs. 1,2.

ACKNOWLEDGMENTS

This work was supported by Polish Government (KBN) Grant No. 2 P03B 148 14. Support of the Polish Academy of Sciences in the framework of Scientific Cooperation Agreements with Consiglio Nazionale delle Ricerche, and with Ukrainian Academy of Sciences is also gratefully acknowledged. The authors wish to express their gratitude to Roman Sobolewski for careful reading of the manuscript and helpful comments.

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[1] H. U. Habermeier, X. H. Li, P. X. Zhang, and B. Leibold, Solid State Commun. **110**, 473 (1999).

[2] D. P. Butler, Z. Celik-Butler, R. Adam, and R. Sobolewski, J. Appl. Phys. **85**, 1075 (1999).

[3] V. D. Okunev, Z. A. Samoilenko, V. M. Svistunov, A. Abal'oshev, E. Dynowska, P. Gierłowski, A. Klimov, and S. J. Lewandowski, J. Appl. Phys. **85**, 7282 (1999).

[4] D. P. Butler, Z. Celik-Butler, and R. Sobolewski, in *Handbook of Advanced Electronic and Photonic Materials* (Academic Press, New York, 2000).

[5] H. Humliček, M. Garriga, and M. Cardona, Solid State Commun.

67, 589 (1988).

[6] D. E. Aspnes and M. K. Kelly, IEEE J. Quantum Electron. **25**, 2378 (1989).

[7] Ivan Bozovic, Phys. Rev. B **42**, 1969 (1990).

[8] H. Yasuoka, H. Mazaki, T. Terashima, and Y. Bando, Physica C **175**, 192 (1991).

[9] D. Salamon, Ran Liu, M. V. Klein, M. V. Karlow, S. L. Cooper, S-W. Cheong, W. C. Lee, and D. M. Ginsberg, Phys. Rev. B **51**, 6617 (1995).

[10] Katsuyoshi Kakinuma and Kazuo Fueki, Phys. Rev. B **56**, 3494 (1997).

[11] V. I. Kudinov, A. I. Kirilyuk, N. M. Kreines, R. Laiho, and E. Ldhderanta, Phys. Lett. A **151**, 358 (1990).

[12] G. Yu and A. J. Heeger, Int. J. Mod. Phys. B **7**, 3751 (1993).

[13] C. Stockinger, W. Markowitsch, W. Lang, W. Kula, and R. Sobolewski, Phys. Rev. B **57**, 8702 (1998).

[14] R. Sobolewski, R. Adam, W. Kula, W. Markowitsch, C. Stockinger, W. Göb, and W. Lang, IEEE Trans. Appl. Supercond. **7**, 1632 (1997).

[15] J. Konopka, V. D. Okunev, Z. A. Samoilenko, S. J. Lewandowski, A. Abal'oshev, I. Abal'osheva, A. Klimov, P. Gierłowski, and S. Barbanera, Proceedings of the 6th International Conference on Materials and Mechanisms of Superconductivity and High Temperature Superconductors, 2000, Houston [Physica C (to be published)].

[16] R. K. Singh and J. Narayan, Phys. Rev. B **41**, 8843 (1990).

[17] S. Otsubo, T. Minamikawa, Y. Yonezawa, A. Morimoto, and T. Shimizu, Jpn. J. Appl. Phys. **29**, L73 (1990).

[18] V. D. Okunev and Z. A. Samoilenko, Tech. Phys. Lett. **24**, 6 (1998).

[19] L. V. Keldysh, Sov. Phys. JETP **33**, 994 (1957).

[20] W. Franz, Z. Naturforsch. A **13**, 484 (1958).

[21] F. Urbach, Phys. Rev. **92**, 1324 (1953).

[22] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[23] P. W. Anderson, Science **235**, 1196 (1987).

[24] C. M. Varna, S. Scmitt-Rink, and A. E. Ruchenstein, Solid State Commun. **62**, 681 (1987).

[25] N. F. Mott and E. Davis, *Electron Processes in Non-crystalline Materials* (Clarendon Press, Oxford, 1979).

[26] V. D. Okunev and Z. A. Samoilenko, Sov. Phys. Solid State **33**, 1588 (1991).

[27] V. N. Variukhin, V. D. Okunev, and Z. A. Samoilenko, Tech. Phys. Lett. **25**, 72 (1999).