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MISFIT STRESSES IN $YBa_2Cu_3O_{7-x}$ FILMS

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Misfit and thermoelastic stresses in HTSC layers 1–2–3 grown on various substrates are analyzed with the use of ultrasonic measurements of Young's moduli in $YBa_2Cu_3O_{7-x}$. *It is shown that the misfit stress gives the main contribution to the formation of the HTSC layer strain.*

At present practical applications of the high-temperature superconductivity phenomenon is significantly limited by the lack of high-quality layers of high-temperature superconductors (HTSC). Their production process is limited by a number of factors, one of which is the lack of substrates with fit structural and physical properties. In the present work, magnitudes of mechanical stresses at the interface between the substrate and the $YBa_2Cu_3O_{7-x}$ layer and their influence on the properties of the layer are evaluated.

The main method of preparation of $YBa_2Cu_3O_{7-x}$ layers is their thermal deposition in vacuum on various dielectric substrates (Table 1) [1–3]. Layers of this material have a thickness of approximately 1 μm and a textured structure with porosity close to zero and are characterized by high dislocation density $N \approx 10^6$–10^9 cm^{-2}, which is much higher than, for example, for films in semiconductor heterostructures fit with their substrates (where $N \approx 10^3$–10^5 cm^{-2}). The influence of the substrate properties on the structural perfection of $YBa_2Cu_3O_{7-x}$ films was pointed out in [1–3]. Thus, cracks were observed in films deposited on substrates prepared from Al_2O_3 or MgO (the difference between the linear expansion coefficients of the HTSC layer and the substrate was $\Delta\alpha = 5.6 \cdot 10^{-6}$ K^{-1}), whereas they did not arise in layers prepared by a similar method and deposited on CrAlY substrates ($\Delta\alpha = 0.4 \cdot 10^{-6}$ K^{-1}) [2].

As experience on the preparation of perfect semiconductor heterostructures has shown, when the build-up layer (l) and the substrate (s) have identical crystal structures, the main factors determining the degree of perfection of the layer are the differences between their crystal lattice parameters

$$\Delta a = a_l - a_s$$

and their linear thermal expansion coefficients $\Delta\alpha = \alpha_l - \alpha_s$ [4].

For large differences between the parameters Δa, misfit stresses arise in layers, and thermoelastic stresses arise for large values of $\Delta a \cdot \Delta T$. Direct estimation of stresses on the interface between the HTSC layer and the substrate is impossible by this scheme, because of misfit structures of the materials in contact: crystalline materials with predominantly cubic symmetry of the lattice (Table 1) are used as substrates, whereas the superconductor film is a polycrystal. Nevertheless, we can approximately estimate the stresses in the isotropic approximation. In this approximation, the elastic properties of the medium are determined by Young's modulus E and the Poisson coefficient ν, and the stress at the layer-substrate interface σ can be represented in the form [4]

$$\sigma = E \cdot f \cdot (1 - \nu), \tag{1}$$

where $f = \Delta a / a$. However, the values of Young's modulus and the Poisson coefficients are unknown for $YBa_2Cu_3O_{7-x}$. The present work is aimed at their determination and evaluation on the basis of magnitudes of stresses at the interface between the crystal substrate and the HTSC layer. Absolute values of E and ν can be determined experimentally (if high-quality polycrystalline samples are available) or calculated (see below) from Young's moduli of $YBa_2Cu_3O_{7-x}$ monocrystals.

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TABLE 1. Lattice parameters, linear expansion coefficients α, misfit between the parameters of the film and the substrate $\Delta a/a$, and linear thermal expansion (for the synthesis and working temperature difference) for $YBa_2Cu_3O_{7-x}$ and various substrates

Material	Crystal structure	Lattice parameter a, nm	$\alpha, 10^{-6}\ K^{-1}$	$\Delta a/a$	$\Delta a \cdot \Delta T$
$YBa_2Cu_3O_{7-x}$	Rhombic (close to tetragonal)	$a = 0.382$ $b = 0.388$	10–15		
MgO	Cubic	0.211	13.8	0.43 (8 % actually)	0.00014
ZrO_2 (doped by 2.5–9% Y_2O_3)	Cubic	0.364		0.093	
$LaGaO_3$	Cubic	0.389	10	0.018	0.00252
$LaAlO_3$		0.379		0.0079	0.00252
Al_2O_3	Hexagonal	$a = 0.476$ $b = 1.290$	7.5–8	0.197	0.00392
Si	Cubic	0.543	2–4	0.29	0.00672
$MgAl_2O_4$	Cubic	0.8059	7.6	0.526	0.00420
$SrTiO_4$	Cubic	0.3905	9.4–10.4	0.022 (0.2–2% actually)	0.00252

TABLE 2. Elastic constants c_{ij} (hPa) of $YBa_2Cu_3O_{7-x}$ monocrystals

Reference	c_{11}	c_{33}	c_{44}	c_{12}	c_{66}
7	211	159	33–36		
8	234	145			
9			25		
10				66	80
11		156	32.2		

The procedure of averaging of Young's moduli for crystals with tetragonal symmetry was suggested in [5]. It allows Young's modulus E and the Poisson coefficient ν to be calculated from Young's moduli of monocrystals c_{ij} in the following form:

$$S_1 = -\nu/E,\ S_2/2 = (1+\nu)/E,$$

$$S_1 = \frac{-3(2c_{11}+c_{33}-4c_{44}+4c_{12}+8c_{13}-2c_{66})}{(2c_{11}+2c_{33}+12c_{44}-4c_{13}-2c_{12}+6c_{66})(2c_{11}+c_{33}+4c_{13}+2c_{12})}, \tag{2}$$

$$S_2/2 = 15/(4c_{11}+2c_{33}+12c_{44}-4c_{13}-2c_{12}+6c_{66}).$$

For calculations by Eq. (2), we used in the present work the values of c_{ij} for the elastic $YBa_2Cu_3O_{7-x}$ parameters measured by ultrasonic methods for the monocrystals presented in Table 2.

The results of calculations by formulas (2) yield the following values:

$$E = 139 \pm 8\ \text{hPa},$$

$$\nu = 0.287 \pm 0.017.$$

Another method of determining Young's modulus and the Poisson coefficient is based on the use of their relationships with longitudinal and transverse components of sound velocity in polycrystals. The data on longitudinal and transverse components of sound velocity in $YBa_2Cu_3O_7$ ceramics with various porosity are collected in [6]. Their recalculation with porosity approaching zero and their subsequent averaging yield the following longitudinal and transverse components of sound velocity in $YBa_2Cu_3O_7$:

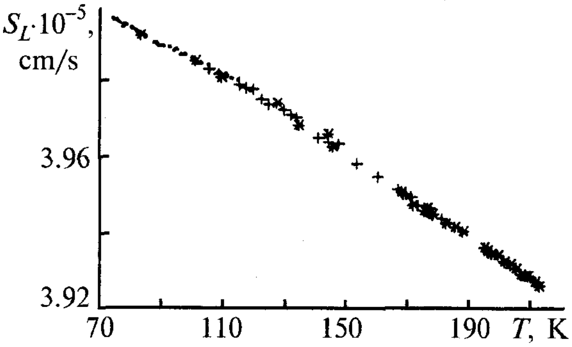

Fig. 1. Temperature dependence of sound velocity in $YBa_2Cu_3O_7$ ceramics with 2% porosity.

$$V_l = (4490 - 230)\ \text{m/s},$$

$$V_t = (2770 - 120)\ \text{m/s}.$$

Using these values and the well-known relations for an isotropic medium:

$$\rho \cdot (V_l)^2 = c_{11},\ \ \rho \cdot (V_t)^2 = (c_{11} - c_{12})/2,$$

$$s_{11} = c_{11} /(c_{11}^2 - c_{12}^2),\ \ s_{12} = c_{12}/(c_{11}^2 - c_{12}^2), \tag{3}$$

$$E = 1/s_{11},\ \ \nu = -E \cdot s_{12},$$

we obtained by this method the following data:

$$E = 121 \pm 12\ \text{hPa},\ \nu = 0.238 \pm 0.012.$$

Thus, it can be seen that the maximum value of Young's modulus for $YBa_2Cu_3O_7$ polycrystals, calculated in the approximation of an isotropic medium, coincides with the minimum value obtained for monocrystals (see above).

It should be noted that neither experimental nor calculated values of Young's moduli and the Poisson coefficients alone can be considered reliable, because the moduli measured for polycrystals depend strongly on the quality of the material, whereas their calculated values neglect this dependence. For this reason, we performed both the direct measurements of E and ν and the calculations within the framework of the well-known approximation. For high-quality ceramic materials, Young's modulus and the Poisson coefficient can be measured directly. In this connection, we measured the elastic parameters of high-quality polycrystalline $YBa_2Cu_3O_7$ samples (with dimensions 2×11×11 mm and porosity less than 3%) at temperatures between 4.2 and 300 K. The critical current at 77.3 K was no less than $J_c = 12$ A/mm^2. The resonance contactless technique of electromagnetoacoustic transformation [12] in the frequency range 0.1–10 MHz was used. The registration of the resonant frequency of standing acoustic (one longitudinal and one transverse) waves on the thickness of a disk has allowed us to measure the velocities of longitudinal (V_l) and transverse (V_t) waves with accuracy no worse than 1%. The temperature dependence of sound velocity (Fig. 1) has no specific features characteristic of low-quality HTSC ceramics, and its monotonic behavior was close to that for monocrystals [11]. The recalculation of sound velocities by formulas (3) has allowed the following experimental Young's modulus and the Poisson coefficient to be obtained (for the data recorded at 300 K)

$$E = 148 \pm 2\ \text{hPa},\ \ \nu = 0.255 \pm 0.003,\ \ E/(1 - \nu) = 199 \pm 10\ \text{hPa}.$$

These experimental results are close to the above-presented elastic $YBa_2Cu_3O_7$ parameters calculated for models [5] and [6].

The proximity of calculated and experimental Young's moduli and Poisson coefficients allows the stress at the interface between the HTSC layer and the substrate to be reliably estimated in isotropic approximation (1). Estimated stresses

TABLE 3. Misfit stresses in the layers of $YBa_2Cu_3O_7$–$BaZrO_3$–YSZ–Al_2O_3 heterostructure

Layer	$YBa_2Cu_3O_7$	$BaZrO_3$	YSZ
Lattice parameters, nm	$a = b = 0.29$ $c = 1.7$	$a = 0.29$ $c = 0.38$	$a = 0.29$
σ, hPa	6.2	5.0–6.2	3.0–5.0

for the structures show that $YBa_2Cu_3O_7$ films (1–2–3) deposited on substrates tabulated in Table 1 are subjected to misfit stresses exceeding 10 hPa. This is primarily due to a significant misfit between the lattice parameters in the basal plane between the HTSC layer and the substrate. Apparently, because of significant misfit stresses, the growing layer has island regions; monocrystal $YBa_2Cu_3O_7$ layers practically cannot be grown for the given substrate types. Moreover, in a number of experiments [2], the HTSC layer integrity was broken. For such films the main mechanism of generation of mechanical stresses is the misfit between the parameters of the film and substrate, whereas the difference between the temperature expansion coefficients is apparently of secondary importance.

The well-known method of reducing mechanical stresses in a semiconductor heterostructure consists in the use of intermediate (fitting to the lattice parameter) layers which decrease elastic stresses in the case of significant misfit between the lattice parameters of the layer and the substrate. The same method was also used for HTSC layers. For example, the YSZ layer (ZrO_2 stabilized by yttrium) was used as a buffer layer in [13], which significantly improved the film structure. Our calculations show that the use of YSZ as a fitting layer reduces stresses at the interface down to 3–5 hPa. Table 3 gives the calculated mechanical misfit stresses in the actual $YBa_2Cu_3O_7$–$BaZrO_3$–YSZ–Al_2O_3 structure.

Eibl *et al.* [13] detected the formation of the intermediate $BaZrO_3$ layer with thickness 2–4 nm in the YSZ buffer layer. Its origin is associated with mutual diffusion of the compounds. This phenomenon should be taken into account when analyzing the properties of the layer-substrate interface. The diffusion of the compounds in the structure may lead to the loss of superconducting properties of $YBa_2Cu_3O_7$. Thus, the migration of Ba and Cu ions toward the interface was pointed out in [1]. To prevent this phenomenon, buffer Au, ZrO_2, and MgO layers were deposited on the substrate. In [3], where $YBa_2Cu_3O_7$ was build on Si, Auger spectroscopy indicated the strong diffusion of Ba and O into the substrate. Harada *et al.* [3] succeeded in the elimination of this effect by using thin buffer ZrO_2 and MgO layers. The formation of transition layers at the film-substrate interface may significantly change the pattern of mechanical stresses in the film structure [14].

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