Ga segregation in DyBa$_2$Cu$_3$O$_{7-\delta}$/PrBa$_2$Cu$_{3-x}$Ga$_x$O$_{7-\delta}$/DyBa$_2$Cu$_3$O$_{7-\delta}$ ramp-type Josephson junctions

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Ramp-type Josephson junctions with highly doped PrBa$_2$Cu$_{3-x}$Ga$_x$O$_{7-\delta}$ barrier layers ($x=0.7$, 1.0) have been investigated by high-resolution electron microscopy. A Ga-rich intergrowth and Ga diffusion in the ion-milled SrTiO$_3$ substrate are observed. The Ga segregation is responsible for the deviating electrical behavior as expected from extrapolation of low doping levels ($x=0.1$–0.4). The Ga diffusion in the ion-milled substrate, and possibly in the base electrode, may hamper Josephson junction fabrication using substituted REBa$_2$Cu$_3$O$_{7-\delta}$ materials (RE=rare earth). © *1997 American Institute of Physics.* [S0003-6951(97)02009-3]

The ramp-type Josephson junctions (JJs) geometry allows adjustment of the junction properties by changing the barrier thickness and/or the barrier material itself. This choice is of great importance to ensure good quality JJs, where the interface resistance should not dominate over the barrier properties. The substitution of Cu in the chain layer by Ga, Co, and Nd in PrBa$_2$Cu$_3$O$_{7-\delta}$ (PrBCO) results in an increase in the bulk resistivity.[1–3]

PrBa$_2$Cu$_{3-x}$Ga$_x$O$_{7-\delta}$ (PrBCGaO) as a barrier layer is expected to produce junctions with a higher normal state resistance R_n than nonsubstituted PrBCO. The substitution of Cu by Ga in ceramic PrBCO was reported by Xu and Guan[1] for substitution levels $0.01 \leq x \leq 0.9$. The maximum substitution level is certainly higher than in the case of Ga substitution for Cu in YBa$_2$Cu$_3$O$_{7-\delta}$ (123) and depends strongly on the rare earth (RE) used.[4]

Targets of PrBCGaO with $x=0.10$, 0.40, 0.70, and 1.00 have been prepared either with citrate synthesis[5] or standard solid-state reactions. All layers of the JJs have been deposited with off-axis rf magnetron sputtering on (001) SrTiO$_3$ substrates.[6,7] The base electrode (DyBCO) and the insulating layer (PrBCO) have been deposited *in situ*. The ramps are structured by an Ar ion-beam source (under an angle of 45°) using a photoresist mask. After stripping the photoresist, the ramp surface is cleaned by ion milling. Without breaking the vacuum, the sample is transported into the sputtering chamber and heated at 790 °C for 1 h in 10 Pa oxygen pressure to achieve reoxygenation of the surfaces. Subsequently, the barrier layer (PrBCGaO) and the top electrode (DyBCO) are deposited. The Ga content of the barrier layer is nominally taken from the target composition. High-resolution electron microscopy (HREM) and electron diffraction (ED) investigations on cross-section samples are performed with a Jeol 4000 EX and a Philips CM 20 microscope.

Electrical measurements of ramp-type JJs with PrBCGaO barriers ($x=0.1$ and 0.4) have been reported previously.[6,8] The effect of Ga substitution in the PrBCO barrier layer on the junction parameters is an increase in the resistivity up to an order of magnitude, whereas the influence on J_c is negligible. However, this trend is not continued for the higher substitution levels. Figure 1 shows the critical current density J_c versus the R_nA product (A, the area of the junction) for ramp-type junctions with Ga-doped PrBCO barriers up to $x=1.0$. For all doping levels J_c is basically unaffected, where R_n decreases for doping levels $x>0.4$ resulting in a reduction in I_cR_n product with respect to $x=0.4$. This unexpectedly low R_n value was the principal reason for investigating possible Ga segregation at high doping levels. Hence, the structure, interfaces, and microstructural defects of these ramp-type JJs were studied by HREM and ED.[9,10] In this letter we concentrate on the particularities in the PrBCGaO barrier layer. The junction, discussed here have a ramp angle of 20°–28° and a barrier layer thickness of 10–30 nm. All layers grow with c-axis orientation perpendicular to the substrate. All interfaces in the nonetched part and in the etched part are sharp and flat. The interfaces between barrier and superconducting layers at the ramp edge are well defined and free of secondary phases or amorphous layers.

X-ray diffraction (XRD) shows that the bulk PrBCGaO samples have a structure identical to tetragonal 123. No Ga-
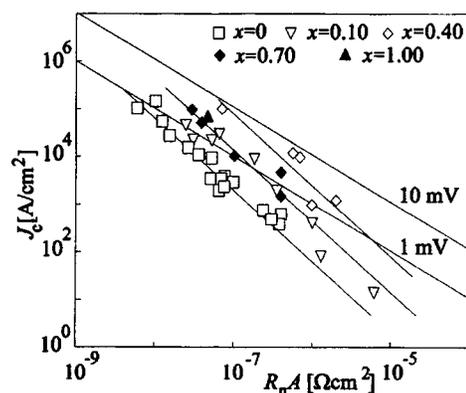
FIG. 1. The critical current density J_c versus the product of normal-state resistance R_n and junction area A, for ramp-type junctions with PrBa$_2$Cu$_{3-x}$Ga$_x$O$_{7-\delta}$ barriers with $x=0.01$, 0.4, 0.7, and 1.0. No increase in resistivity for $x=0.7$ and 1.0 compared to $x=0.4$ was observed.

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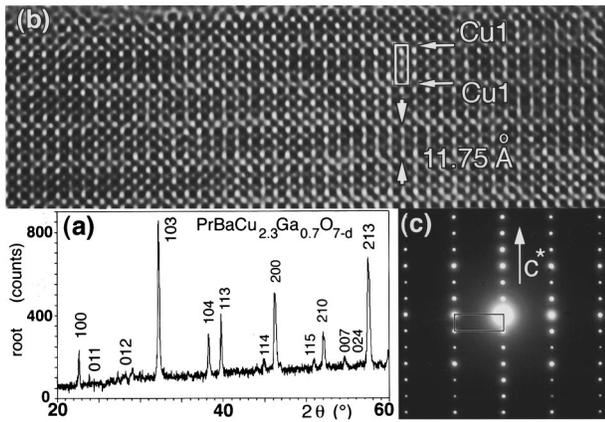
FIG. 2. Bulk target $PrBa_2Cu_{2.3}Ga_{0.7}O_{7-\delta}$, (a) monophase XRD plot, (b) large defect-free domains of the tetragonal 123 structure imaged along [100] and (c) corresponding ED pattern.

FIG. 3. (a) Overview of a 30 nm $PrBa_2Cu_{2.3}Ga_{0.7}O_{7-\delta}$ barrier layer with non-123 unit cells indicated by double arrows. These arrange locally in a stacking sequence $[c_{123}]_3[c_i]_1$. (b) Model of the Ga-intergrowth cell based on the structure of $PrSrGaCuO_5$.

containing impurity phases are present in PrBCGaO with $x=0.7$ [Fig. 2(a)]. The unit cell parameters, $a=0.39288(6)$ nm and $c=1.1756(5)$ nm, are in good agreement with Xu and Guan.[1] ED experiments show no extra spots nor streaks. HREM along the [100] direction [Fig. 2(b)] and corresponding ED pattern [Fig. 2(c)] revealed a perfect 123 structure over large areas without inclusions or intergrowths and confirm the c/a ratio of 2.99. There is no modulation or structural change of the 123 structure, as detectable by EM, due to the Ga substitution in the Cu(1) chain.

The HREM image of Fig. 3(a) shows part of a 30 nm thick PrBCGaO barrier layer ($x=0.7$) grown on the ion-milled substrate. The barrier layer contains isolated unit cells with c-axis lengths different from $c_{123}\approx1.17$ nm, indicated by double arrows, throughout its complete thickness. These unit cells, with lattice constant $c_i\approx0.8$ nm, are not known as common defects in 123. They are perfectly intergrown and often occur periodically within the 123 structure. Such a regular stacking sequence consists of three unit cells of 123 with spacing c_{123} and one intergrowth with spacing c_i. The periodicity of this $[c_{123}]_3[c_i]_1$ sequence is 4.3 nm. The intergrowth occurs only in the PrBCGaO barrier layer, not in the DyBCO bottom or top layer nor in the PrBCO insulating layer. The regular stacking sequence $[c_{123}]_3[c_i]_1$ occurs for $x=0.7$. If the Ga content is increased ($x=1.0$) the frequency of the c_i slabs in the stacking is increased and sequences such as $[c_{123}]_2[c_i]_1$ or $[c_{123}]_1[c_i]_1$ can be observed. The

presence of Ga seems to enhance the formation of intergrowths. The observed lattice parameters could not be identified as oxides containing Ga, Pr, Ba, and Cu given in powder diffraction files. The contrast of the intergrowth strongly resembles a double perovskite with an inequivalent lattice plane in the middle of the cell. This, together with the frequency of the intergrowth slab as a function of the substitution level, is interpreted as the occurrence of a full Ga plane. Subsequently, a model for the Ga containing intergrowth layer is proposed. This model is based on $PrSrGaCuO_5$ with lattice parameters $a=1.63358$ nm, $b=0.55002$ nm and $c=0.53534$ nm (spacegroup $Ima2$).[11] The tetrahedral oxygen coordination of Ga induces shifts of the Ga and O atoms away from the ideal perovskite positions. The contrast of the intergrowth cell can be matched with simulations of the model of Fig. 3(b) for various defocus and thickness values.

Figure 4 shows the interface region between the barrier layer and the ion-milled $SrTiO_3$ substrate. In the upper most 10 nm of the substrate, pronounced black patches, indicated by arrows, are observed. The $SrTiO_3$ lattice in the dark contrast areas is distorted. This is clearly visible under grazing angle, see the inset of Fig. 4. However, no dislocations can be observed. This specific contrast exists in all parts of the
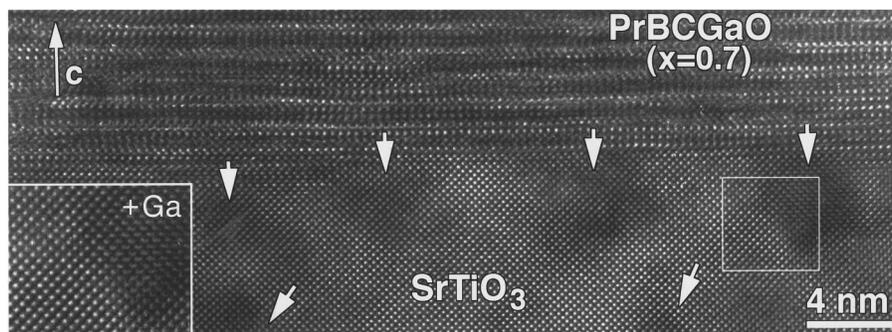
FIG. 4. [001] HREM micrograph of the interface between $PrBa_2Cu_{2.3}Ga_{0.7}O_{7-\delta}$ and ion-milled $SrTiO_3$. Dark contrast areas in the substrate are indicated by arrows. The inset shows the distorted lattice image at a higher magnification.
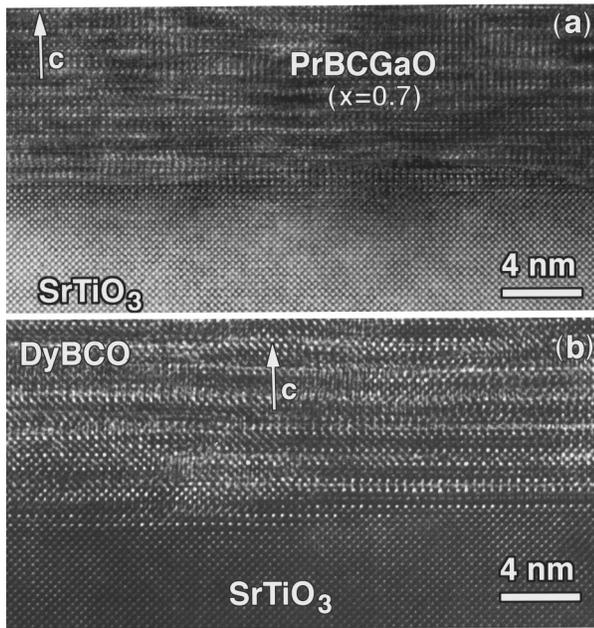
FIG. 5. [001] HREM micrograph of (a) the interface between $PrBa_2Cu_{2.3}Ga_{0.7}O_{7-\delta}$ and pristine $SrTiO_3$ and (b) the interface between $DyBa_2Cu_3O_{7-\delta}$ and ion-milled $SrTiO_3$. Both are free of dark contrast areas.

$SrTiO_3$ substrate, which has been exposed to Ar milling to create the ramp edges, even on the inclined ramp edge in $SrTiO_3$. Such contrast variations are normally not observed for REBCO films on $SrTiO_3$ and is not observed in the non-etched part of the junction. This rules out ion-beam thinning for HREM specimen preparation as the possible origin. Possible other causes are oxygen depletion and interdiffusion of either photoresist or Ga from the barrier layer. Fig. 5(a) shows a [100] HREM image of the interface between PrBCGaO ($x=0.7$) and pristine $SrTiO_3$, whereas in Fig. 5(b) the interface of a DyBCO layer on an ion-milled $SrTiO_3$ substrate is shown. The particular contrast of black patches, which only exists in Fig. 4 and is absent in Figs. 5(a) and 5(b), is related to the combination of a Ga-containing REBCO layer on an ion-milled $SrTiO_3$ substrate. Only ion milling is insufficient to produce this contrast. We suppose that Ga diffusion in the surface region of the ion-milled $SrTiO_3$ substrate is the origin of the local structural distor-

tions. This can be understood if we assume that lattice imperfections, such as oxygen vacancies or point defects, created during ion-milling, facilitate the diffusion of Ga in the interface region of the substrate. Because the Ga diffusion is detected in the ramp area as well, the use of ion-beam milling together with highly substituted barrier layers can hamper future JJ fabrication. Diffusion of the Ga in the base electrode could not be observed but cannot be excluded as well.

The behavior of the junction parameters at high Ga-substitution levels is better understood due to the HREM characterization. The microstructure of $PrBa_2Cu_{3-x}Ga_xO_{7-\delta}$ ($x=0.7,1.0$) thin barrier layers is clearly different from the one in bulk material. A Ga-rich intergrowth was detected in the barrier layers together with the diffusion of Ga in the ion-milled substrate. Thus, two distinct mechanisms of Ga segregation in thin barrier layers are operative and render high Ga-substitution levels ineffective to enhance the normal-state resistivity.

[1] Y. Xu and W. Guan, Physica C **206**, 59 (1993).
[2] G. Koren, E. Polturak, G. M. Reisner, B. Fisher, and L. Patlagan, Physica C **225**, 21 (1994).
[3] C. T. Rogers, A. Inam, and R. Ramesh, IEEE Trans. Magn. **27**, 1600 (1991).
[4] T. A. Mary, N. R. S. Kumar, and U. V. Varadaraju, J. Solid State Chem. **107**, 524 (1993).
[5] D. H. A. Blank, H. Kruidhof, and J. Flokstra, J. Phys. D **21**, 226 (1988).
[6] M. A. J. Verhoeven, G. J. Gerritsma, H. Rogalla, and A. A. Golubov, IEEE Trans. Appl. Supercond. **5**, 2095 (1995).
[7] M. A. J. Verhoeven, G. J. Gerritsma, and H. Rogalla, Inst. Phys. Conf. Ser. **148**, 1395 (1995).
[8] M. A. J. Verhoeven, G. J. Gerritsma, H. Rogalla, and A. A. Golubov, Appl. Phys. Lett. **69**, 849 (1996).
[9] K. Verbist, O. I. Lebedev, G. Van Tendeloo, M. A. J. Verhoeven, A. J. H. M. Rijnders, and D. H. A. Blank, *Proceedings of the European Conference on Electron Microscopy XI*, EUREM '96 (UCD Bellfield, Dublin, 1996).
[10] K. Verbist, O. I. Lebedev, G. Van Tendeloo, M. A. J. Verhoeven, A. J. H. M. Rijnders, and D. H. A. Blank, Supercond. Sci. Technol. **9**, 978 (1996).
[11] G. Roth, P. Adelmann, R. Knitter, S. Massing, and T. Wolf, J. Solid State Chem. **99**, 376 (1992).