Preparation of BiSrCaCuO thin films by atomic layer-by-layer molecular-beam-epitaxy and high-resolution transmission electron microscopy analysis of the film/substrate interface and of growth defects


Abstract

By means of atomic layer-by-layer molecular-beam-epitaxy (MBE) we have prepared BiSrCaCuO thin films and vertical S–N–S (2212/2201/2212) junctions on SrTiO₃ and LaAlO₃ substrates at 720 °C in 2×10⁻⁵ mbar ozone pressure. 40 nm thick Bi-2212 films show an inductively measured Tc of 84 K. The period of RHEED intensity oscillations, observed during growth, is correlated with the growth of half a unit cell. By means of HRTEM we have investigated the defect structure of the atomic layer-by-layer grown films. The films contain twins and interfacial dislocations, and some precipitates. Most prominent are Bi-rich precipitates of various size. Interfacial dislocations were found to be located in the films at a distance of up to 3 nm from the film/substrate interface. The analysis showed that the film/substrate interface in the films is considerably sharper and has a better planarity, if the layer-by-layer MBE process starts with a Sr–O layer instead of a Bi–O layer.

Keywords: Thin-films; Molecular beam epitaxy; High-resolution tunnelling electron microscopy analysis

1. Introduction

For high-temperature superconductor (HTSC) weak links, one needs techniques to prepare barriers of the order of magnitude of the coherence length, i.e. in the order of a few nm. Examples are step-edge- and bi-crystal-junctions. An alternative method is the preparation of vertical planar weak links such as S–N–S or S–I–S junctions. For this purpose the surface roughness has to be minimal to avoid shorts between the superconducting layers through the very thin inhomogeneous barrier. In our view, first choice for preparing very smooth surfaces is the molecular-beam-epitaxy (MBE). Moreover, the atomic layer-by-layer deposition offers a great potential for unit-cell synthesis.

2. Preparation

We have prepared BiSrCaCuO thin films and vertical S–N–S junctions by atomic layer-by-layer MBE in an atmosphere of highly enriched ozone of 2×10⁻⁵ mbar, similar to Ref. [1,2]. The MBE system consists of two sections linked via a cone with an 8 mm aperture, in order to provide differential pumping. This is necessary for obtaining a high ozone pressure for the oxidation of the metals near the substrate, but conserving the low pressure in the evaporation section of the chamber. There are up to six shutter-controlled evaporation sources for the four constituents of the BiSrCaCu system and two for further doping materials. Thin films were prepared by evaporation of one element after the other in the sequence of the atomic layers in the Bi₂Sr₂Ca₂Cu₃O₈₋ₓ unit cell. Vertical thin film junctions were made as S–N–S sandwiches or prepared through a 5×1.5 mm slit-mask (Fig. 1), with Bi-2201 as barrier material.

During deposition, the intensity of RHEED spots was observed and showed different behavior for the Bi-2212 and Bi-2201 deposition sequences (Fig. 2). During the Bi-2212 sequence, a periodic oscillation could be seen. The oscillation period was correlated with the growth of half a unit cell. The growth of the Bi-2201 sequence showed no periodic intensity variations. The second Bi-2212 layer behaved similar to the first one.

3. Properties of the thin films and the S–N–S junctions

Bi-2212 films of 40 nm thickness, deposited on SrTiO₃ substrates at a substrate temperature of 720 °C, showed an inductively measured Tc of 84 K. X-Ray diffraction and
2\Delta/k_B T_c to 3.7\pm0.2 at 4 K with a non-BCS-like linear temperature dependence for 5\leq T \leq 50 K.

4. HRTEM bulk and interface investigations

The HRTEM investigations of a MBE-film with a high Sr content, such as Bi_{2}Sr_{2-x}Ca_{x}Cu_{3}O_{y}, showed certain lamellae-like distortions of the structure. These distortions may be attributed to a substitution of Sr for Ca because of the difference in the ionic radii. Image contrast simulations [3] using an ideal Bi_{2}Sr_{2}Ca_{x}Cu_{3}O_{y} crystal compared to a crystal where the Ca atoms were replaced by Sr atoms, yield good agreement.

We found two different kinds of precipitates in the MBE-films. Fig. 4 shows an image of a large precipitate marked "A". According to EDX, these precipitates are Bi-rich, containing almost no copper. Their composition is close to Bi_{2}Sr_{2}Ca_{x}Cu_{3}O_{y}, which was observed in the Bi_{2}O_{3}-SrO-CaO-CuO system at 850°C [4]. A different kind of small precipitate was observed in plane-view images. They are about 15 nm in diameter, which is too small for an EDX analysis, but the rather high contrast of the Moiré fringes, despite the small particle size, suggests a high atomic number and therefore they probably consist of bismuth oxide or are at least rich in Bi. Only the sample grown on LaAlO_{3} substrate shows additionally a precipitate, with the composition near Sr_{0.66}Ca_{0.33}CuO_{2}. The wavelength \lambda of the incommensurate modulation along the b-axis (Fig. 4) varies from place to place between 2.63 and 2.48 nm. According to our previous observations and to STM observations at the surface of the film [5], the wavelength varies with the oxygen content. The STM results are: \lambda=2.48 nm for optimally or overdoped films and \lambda=2.71 nm for underdoped films.

Two samples were grown on SrTiO_{3}-substrates to identify the influence of the first evaporated layer onto the structure of the interface. According to the HRTEM observations (Fig. 5(a-b)), the film/substrate interface was considerably sharper and had a better planarity if the growth was started with a Sr-O layer as compared to interfaces of samples started with a Bi-O layer.

The misfit accommodation along the film/substrate will influence the quality of the interface. In the MBE films the interfacial dislocations, accommodating the film/substrate misfit, are always up to 3 nm away from the interface [3]. For a dislocation, it is energetically favorable to stay between two weakly bonded layers, i.e. in this case between the Bi--O double layer [6]. Since the Bi--O layers of the film are not the first layers to grow, this energetic preference explains well the observed distance of the dislocation from the film/substrate interface.

Most remarkable is that the film/substrate misfit is a function of the Sr/Ca ratio in the MBE-grown film. A film with a high Sr-content was perfectly lattice matched to the SrTiO_{3} substrate. This implies the possibility of growing lattice-matched films by varying the Sr content, as...
Fig. 3. $dI/dU$ characteristic of a vertical S–N–S junction. The structures at ±20 meV are due to the energy gap.

it is known for different lattice-matched semiconductor films, such as Al$_x$In$_{1-x}$As on GaAs.

Fig. 6 shows a HRTEM investigation of a S–N–S junction (for preparation see Section 2). The numbers $n=1, 2, 3, 4$ at the right denote the stoichiometry of the Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{4+n+δ}$ compound. The interface quality of the S–N–S junction is of good enough quality to allow a further reduction of the barrier (Bi-2201) thickness. With a reduced barrier thickness a Josephson-current through the junction will be observable.

5. Conclusion

Thin films and S–N–S junctions of Bi-2212 (S) and Bi-2201 (N) were prepared by atomic layer-by-layer MBE. The period of RHEED intensity oscillations during thin
Fig. 6. HRTEM cross-section image of a MBE-grown vertical S–N–S junction. The numbers denote the number (n) of CuO₂-planes.

film growth is correlated with the growth of half a unit cell. The S–N–S junctions show a quasiparticle tunnelling $dI/dU-U$ characteristic with structures at ±20 meV due to the energy gap. HRTEM showed a partial replacement of Ca by Sr-lamellae. The still existing precipitates in the thin films are mostly Bi-rich. The film/substrate interface is considerably sharper and had a better planarity if the growth was started with a Sr–O layer instead of BiO. In the BiSrCaCuO films, interfacial dislocations occur near the film/substrate interface at a distance of up to 3 nm.

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References