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# Crack formation in $YBa_2Cu_3O_{7-\delta}$ films on silicon

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**Abstract**

Differences in the thermal expansion between epitaxially grown films and the substrate result in a considerable strain of the deposit. Whenever a certain critical film thickness is exceeded the stress is inevitably relaxed by fracture. This problem is most prominent for $YBa_2Cu_3O_{7-\delta}$ films deposited on silicon substrates. We have studied the mechanism of crack formation in more detail, especially the part played by the surface morphology of the $YBa_2Cu_3O_{7-\delta}$ films. Theoretical limits are compared with experimental findings.

## 1. Introduction

A severe but often underestimated problem in hetero-epitaxial film growth at elevated temperatures arises from differences in the thermal expansion coefficients between the film and the substrate material. Because the film has grown in registry to the substrate lattice its thermal contraction during cooling to room temperature is strictly determined by the substrate, at least as long as the film thickness is small compared to the substrate thickness. Although an intermediate epitaxial buffer layer may relax the strain originating from some lattice mismatch at the deposition temperature it can in principle not compensate strain due to differential thermal expansion.

Since the thermal expansion coefficient of $YBa_2Cu_3O_{7-\delta}$ is in general larger than those of standard substrates, $YBa_2Cu_3O_{7-\delta}$ films are strained under normal conditions. Hence, when a certain critical film thickness – given by the amount of strain and the mechanical properties of $YBa_2Cu_3O_{7-\delta}$ – is exceeded, cracks will appear. In this way the effective cross-section of the superconductor is reduced and the electrical transport properties are severely affected.

This problem which is common to any substrate material used so far, is most prominent for $YBa_2Cu_3O_{7-\delta}$ films on silicon. For this reason we have investigated the mechanism and the theoretical and practical limitations of crack formation for this examplary system.

## 2. Film fabrication

The $YBa_2Cu_3O_{7-\delta}$ films employed for this study were deposited on silicon using intermediate buffer layers of $YSZ/Y_2O_3$ [1]. The YSZ buffers were electron-gun evaporated at 780°C in $10^{-4}$ mbar oxygen ambient. After transfer to the $YBa_2Cu_3O_{7-\delta}$ deposition chamber a 6 nm thin $Y_2O_3$ layer was deposited first to improve the quality of the subsequent $YBa_2Cu_3O_{7-\delta}$ film. For the latter we applied the technique of thermal co-evaporation of the metals from three boats [2]. Because the deposition rate of each metal is controlled independently by an own quartz monitor the composition of the film can be varied arbitrarily. We have shown in some previous work that deviations from the ideal stoichiometry even in the range of a few percent are sensitively correlated to the surface morphology of the $YBa_2Cu_3O_{7-\delta}$ films [3][4].

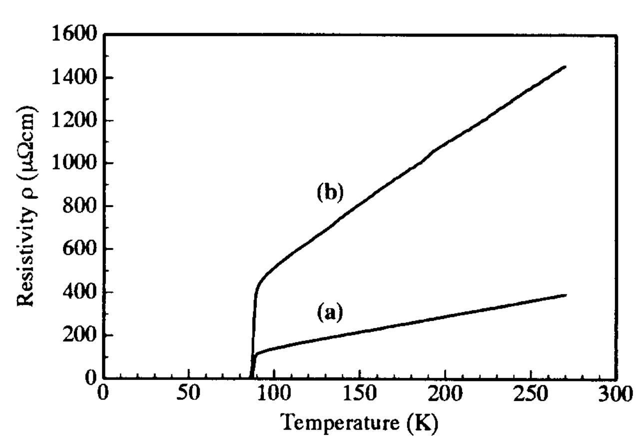


Figure 1. Resistive transitions of $YBa_2Cu_3O_{7-\delta}$ on $Y_2O_3/YSZ/Si$ measured (a) immediately and (b) two days after deposition.The zero resistance temperature of $T_c$ = 87.4 K remained unchanged.

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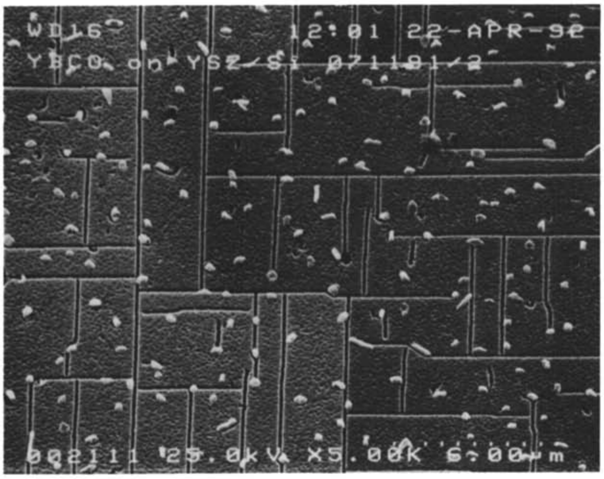


Figure 2. Etched fracture pattern of a 110 nm thick $YBa_2Cu_3O_{7-\delta}$ film on $Y_2O_3$/YSZ/Si with a high density of outgrowth.

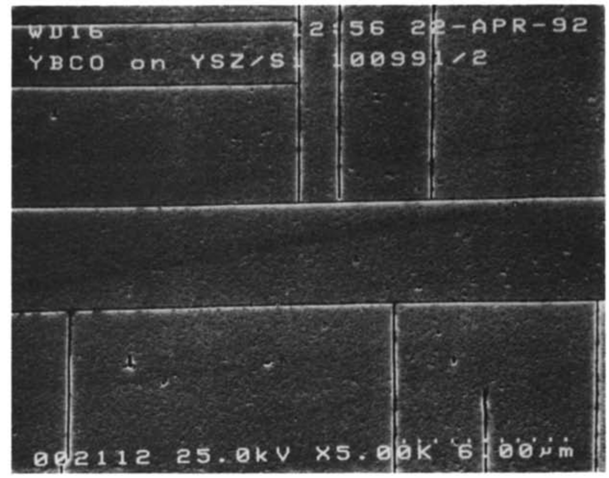


Figure 3. Etched fracture pattern of a 110 nm thick $YBa_2Cu_3O_{7-\delta}$ film on $Y_2O_3$/YSZ/Si with a smooth surface.

The films deposited in this way were epitaxial and exhibited zero resistance temperatures of 87 K. Immediately after removal from the deposition chamber critical transport current densities up to $2.5\cdot10^6$ A/cm$^2$ at 77 K and normal state resistivities as low as 40 $\mu\Omega$cm at 100 K could be measured across Laser-structured bridges using a 1 $\mu$V/mm -criterion.

## 3. Crack formation

However, most samples above a certain critical thickness limit showed a severe degradation in their electrical transport properties within a few days or even hours. The magnetic shielding dropped drastically and the resistive transitions changed in a peculiar way. An example of this behaviour is depicted in Fig.1. Trace (a) was recorded by a standard four point probe immediately after the deposition was completed and the film had cooled to room temperature. In comparison, trace (b) was measured two days later using the same contacts. In either case the normal resistance extrapolates well to zero and the transition temperature has not changed at all. This implies that the intrinsic properties of the superconductor have not been affected. However, the absolute value of the resistivity has increased by a factor of nearly five.

The reason for such a degradation became clear when the samples were examined by field emission scanning electron microscopy (FE-SEM). The whole film was run through by long, about 8 nm wide cracks parallel ⟨100⟩ which were not visible initially. Selective $YBa_2Cu_3O_{7-\delta}$ etching and cross-sections showed that they cut through the whole film thickness even into the YSZ buffer. In this way the current flow within the superconductor is disrupted and the effective cross-section reduced.

The crack density which determines the factor of degradation in $j_c$ and $\varrho$ depends sensitively on the surface morphology of the $YBa_2Cu_3O_{7-\delta}$ films. We have decorated the cracks by bromine etching to observe the fracture patterns on a large scale. In Figs. 2 and 3 two films of equal thickness (110 nm) but different surface quality are compared. The film of Fig.2 has been grown with a surplus of a few percent copper giving rise to typical, irregular outgrowth particles on the surface. Obviously the origins of most cracks are directly correlated with such flaws resulting in an average crack spacing of 2 to 3 $\mu$m. If the copper concentration is reduced, the films become very smooth and the flaw density decreases considerably. Consequently, as shown in Fig.3, the distance between cracks increases up to 5 to 10 $\mu$m.

## 4. Thickness limit

As mentioned above, a certain critical film thickness is needed to render films susceptible to fracture. Knowing the fracture toughness $K_c$ of the film and the stress $\sigma$ effective, it is easily calculated [5].

$$t_{cr} = 0.5\left(\frac{K_c}{\sigma}\right)^2 \tag{1}$$

The tensile stress, in turn, is a result of the thermal expansion mismatch and given by

$$\sigma = 4c_{44}\left(1 - \frac{c_{44}}{c_{11}}\right)(\alpha_{YBCO} - \alpha_{Si})\Delta T \qquad (2)$$

where $c_{11}$ and $c_{44}$ are the elastic moduli of the film and $\alpha_{YBCO}, \alpha_{Si}$ the thermal expansion coefficients. Taking their values ($c_{44}$ = 34.5 GPa, $c_{11}$ = 211 GPa [6], $\alpha_{YBCO} = 16 \cdot 10^{-6}$ 1/°C [7], $\alpha_{Si} = 3.8 \cdot 10^{-6}$ 1/°C [8]) from literature and assuming a temperature difference of $\Delta T = T_s - T_{room} = 620°C$ in our case we arrive at $\sigma$ = 873 MPa. The fracture toughness of $YBa_2Cu_3O_{7-\delta}$ single crystals has been determined by indentation measurements to be $K_c = 0.7$ MPa$\sqrt{m}$ [9]. Applying Eq.1 we obtain a critical thickness of 320 nm which appears surprisingly high. Experimentally, we observed a thickness limit of 70 nm for the vast majority of films which corresponds to a fracture toughness of only 0.33 MPa$\sqrt{m}$.

This implies that the intrinsic mechanical stability of thin $YBa_2Cu_3O_{7-\delta}$ films is poorer than that of single crystals. In fact, $YBa_2Cu_3O_{7-\delta}$ films grown far from equilibrium normally exhibit a much higher density of crystalline defects than single crystals slowly grown from the melt at much higher temperatures [10]. To some extent the different growth conditions may account for the differences in the crystalline quality. On the other hand, however, even slightest deviations from the ideal 1-2-3 stoichiometry inevitably result in lattice imperfections. Such deviations are common to all thin film deposition techniques so that it is extremely hard to achieve films close to the ideal composition within fractions of a percent. In the case of success, however, those films should withstand the stress to the theoretical limit.

As a matter of fact that supports the latter argument we noted some few exceptions from the general rule, namely films up to 120 nm thickness without any cracks even six months after deposition and after bromine etching. Unfortunately, the exact composition of the exceptional films could not be analysed. This is because the most accurate method, heavy ion Rutherford backscattering [4], is affected by the YSZ buffer layer. Nevertheless, from the smooth surface morphology of these films we would estimate a composition very close to the ideal value.

## 5. Conclusions

We have studied the fracture of $YBa_2Cu_3O_{7-\delta}$ films on silicon substrates with $YSZ/Y_2O_3$ buffers. Films up to 70 nm are always crack-free. From this we deduced a fracture toughness which is only half of that of single crystals. The cause may be lattice imperfections and deviations from the stoichiometry in the films. Some perfect films were found to be crack-free up to 120 nm thickness.

This means that even on silicon substrates the thickness limit should not pose restrictions to most applications when the film growth can be perfectly controlled.

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