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Effect of low silicon concentration on high T_c Y–Ba–Cu–O

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The effect of superconductor–semiconductor interaction on the d.c. resistance and a.c. magnetic susceptibility of the prepared samples was recorded. T_c was reduced by increasing Si content, and the superconductivity phase was completely destroyed at an Si:YBCO ratio $\geqslant 2\%$.

1. Introduction

The integration of high-temperature (HT_c) superconductors with conventional semiconductor-based technology could have important consequences for microelectronics, with the promise of high-performance hybrid circuits incorporating the best of what superconductors and semiconductors have to offer, as well as the possibility of novel devices. Adding to the well-known advantages of semiconductors, passive superconductive elements such as transmission lines offer the possibility of low loss, dispersionless signal transmission, while active devices such as Josephson functions make it possible to achieve very fast switching speeds with limited generation of heat.

There has been rapid progress in the fabrication of high-quality HT_c superconductor thin films on substrates such as $SrTiO_3$, MgO and $LaAlO_3$, but results on semiconductors such as Si have been less impressive [1]. Electrotechnical applications of HT_c superconductors require a fabrication of these new 'superconductors' with the older 'semiconductors'. In preparation of HT_c superconductor thin films on semiconducting substrates such as Si, when the conditions require a heated substrate and post-annealing at high temperatures, the quality of the superconducting thin films on Si substrate has not been satisfactory [2]. Similar problems have been also encountered in single-crystal growth of the $Y_1Ba_2Cu_3O_{7-\delta}$ (YBCO) superconductors, which required minimal chemical interactions between the superconductor and boat material [3].

In the present study, results of the investigation of the solid-state interactions between $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors and Si semiconductors with different Si:YBCO ratios by d.c. resistance and a.c. magnetic susceptibility are reported, to clarify the nature of these interactions for possible high-performance superconductor applications.

2. Experimental procedure

2.1. Sample preparation

The starting materials were $Ba(NO_3)_2$, CuO and Y_2O_3 powders, and Si single crystal with a purity over 99.99%. The samples under investigation with the nominal composition $(Y_1Ba_2Cu_3O_{7-\delta})_{1-x}$ Si_x were prepared by the solid-state reaction method by the following steps.

2.1.1. Preparation of barium cuprates

$Ba(NO_3)_2$ and CuO were mixed together to verify the composition $Ba_2Cu_3O_5$, then pressed at 600 kg cm^{-2}, heated at 950 °C for 1 h, cooled at a rate of 150 °C h^{-1}, and finally the resultant material, $Ba_2Cu_3O_5$ was ground.

2.1.2. Preparation of $Y_1Ba_2Cu_3O_{7-\delta}$

$Ba_2Cu_3O_5$ and 1/2 Y_2O_3 were mixed and ground with an electrically vibrating agate mortar type KM1, until a very fine powder of unique colour was observed. The powder was pressed at 600 kg cm^{-2} into pellets (pellets rather than loose powders were used during calcining to minimize contact and interactions between the powder and crucibles). The pellets were calcined in air at 900 °C at a rate of 1000 °C h^{-1}, held at 900 °C for 12 h and cooled to 200 °C at a cooling rate of 150 °C h^{-1}. The sample was then cooled to room temperature in air, and then ground and pressed at 600 kg cm^{-2}. The samples were heated at 900 °C in a flow of airplast for 1 h and left to cool from 100 °C h^{-1} to room temperature. The pellets were finally annealed at 400 °C for 24 h in air to saturate the oxygen requirements for the superconducting state. After the samples were annealed, the pellets were left inside the switched off furnace to return to room temperature. The ingot samples were stored in a dessicator at room to avoid the negative water vapour effects on the samples.

It was reported that a two-step calcination method for preparing superconducting $Y_1Ba_2Cu_3O_{7-\delta}$ results in a narrower particle size distribution, smaller particle sizes and sintered pellets with superior superconducting properties [4] to those prepared by the

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conventional calcination method. Thus the two-step calcination method was used in this study. The prepared $Y_1Ba_2Cu_3O_{7-\delta}$ samples were checked by d.c. resistance and a.c. magnetic susceptibility, showing super-conducting behaviour.

2.1.3. Preparation of suggested compositions

The Si dopant was introduced in the form of single crystal. The $Y_1Ba_2Cu_3O_{7-\delta}$ and Si were mixed together according to the chemical formula: $(Y_1Ba_2Cu_3O_{7-\delta})_{1-x}$-$Si_x$ where $x = 0, 0.5, 1, 2$ and 5%. The mixture was ground with the same agate mortar for approximately 30 min, until a very fine powder of unique colour was observed and pressed into pellets at 600 kg cm^{-2}. The pellets were sintered at 900 °C for 24 h in air and the furnace was switched off to cool the samples slowly to room temperature. Finally the samples were annealed at 400 °C for 24 h in air.

2.2. d.c. Resistance measurements

Electrical resistance was measured by the standard four-probe method, taking account of the following limitations.

(i) Unless the used current was very small (10 mA), the measurements were performed for both current directions in order to eliminate the thermal e.m.f. effects.

(ii) Silver paste electrodes were used to avoid contact effects.

(iii) The leads and the sample were situated on a long probe to enable the current input and the voltage exchanges to be made while the sample was immersed in the liquid-nitrogen dewar.

The current source used was Model 2553 d.c. voltage-current standard, the drop voltage was measured by a Keithely Model 181 Nanovoltmeter, and the temperature was recorded with a calibrated PT-100 thermometer resistance. Both drop voltage and PT-100 resistance were recorded by a computerized program system.

2.3. a.c. Magnetic susceptibility measurements

The a.c. magnetic susceptibility χ (real part) was measured by the double-coil method. A reference a.c. current from the lock-in-amplifier Model SR 530 was selected at a frequency of 105 kHz and used to induce the two coils. The sample was put in one coil and the induced voltage generated was recorded as a function of thermal e.m.f. of a Cr–Al thermocouple with a computerized program.

3. Results

The temperature dependence of the normalized d.c. resistance to the value at 300 K, in the temperature range 78–300 K, is shown in Fig. 1. From inspection of these curves it is noticed that the 1–2–3 phase sample

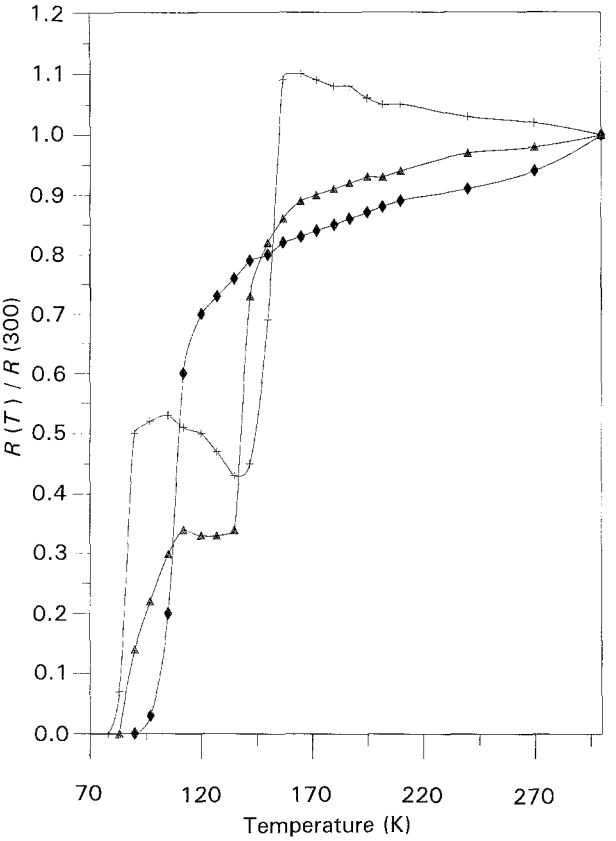

Figure 1 Temperature dependence of the normalized d.c. resistance to the value at 300 K for the $(Y_1Ba_2Cu_3O_{7-\delta})_{1-x}$ Si_x system where x = ◆, 0; ▲, 0.5; + 1%. Samples with Si ratio > 2% are non-superconductors.

with free Si has $T_c = 93$ K. As the Si content increases, T_c reduces, but there is a new phase of superconductivity at $T_c = 135$ K. The addition of more Si to the sample with the ratio Si $\geqslant$ 2% destroyed the superconducting state even at LN temperature. It is also noticed that the room temperature resistance R_{300} was increased by increasing the Si/YBCO ratio; this result is expected from the literature, which demonstrates that more Si atoms lead to increased resistance. The results of a.c. magnetic susceptibility are shown in Fig. 2, confirming the result of d.c. resistance that the transition temperature of the superconducting phase was reduced by adding Si atoms with ratio $\leqslant$ 1%. The samples with Si content $\geqslant$ 2% also show a diamagnetic signal which means that there are still superconductor domains; these domains do not appear in the d.c. conductivity due to weak junctions, and accordingly it is not possible to form a multiconnected network which behaves like a single loop as a whole specimen.

From XRD patterns (Fig. 3) it is clear that the amplitude of the strongest peak of the orthorhombic phase (0 1 3) and (1 1 0), (1 0 3) were decreasing by increasing Si ratio up to Si = 1%. As Si content increased to the ratios 2 and 5%, the peaks of the orthorhombic phase (0 1 3), (1 1 0), (1 0 3) disappeared which means that the samples transformed to a normal conductive state. The calculated cell parameters of the orthorhombic 1–2–3 superconductive phase were $a = 0.383$, $b = 0.389$, $c = 1.170$ nm. By adding Si atoms to the 1–2–3 orthorhombic phase with low

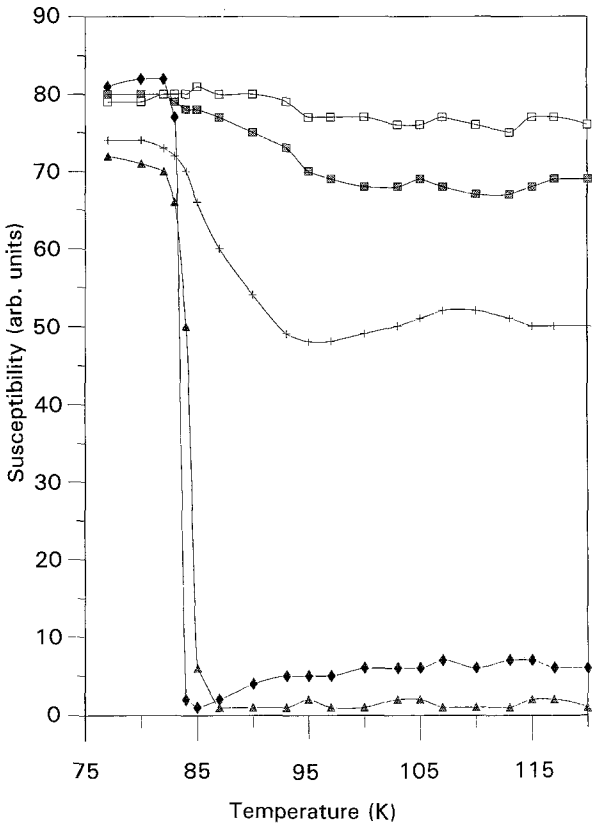

Figure 2 Temperature dependence of the a.c. susceptibility for the $(Y_1Ba_2Cu_3O_{7-\delta})_{1-x}Si_x$ system where x = ◆, 0; ▲, 0.5; +, 1; ■, 2 and □, 5%.

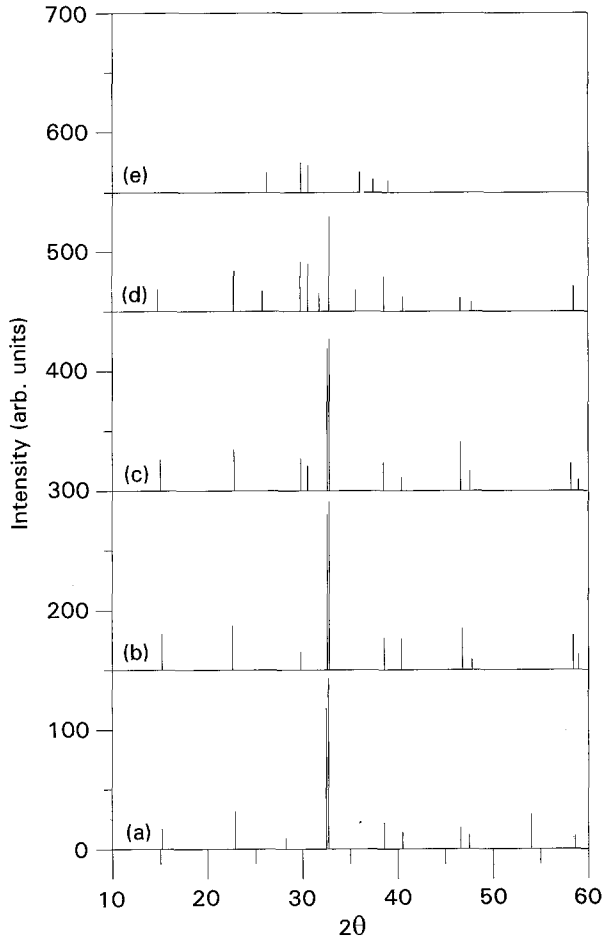

Figure 3 XRD of the $(Y_1Ba_2Cu_3O_{7-\delta})_{1-x}Si_x$ system where x = a, 0; b, 0.5; c, 1; d, 2 and e, 5%.

ratio (Si = 0.5, 1%), new phases (around the strongest peak 103) are present and identified at $d = 0.353$, 0.3109, 0.3062 and 0.2633 nm with corresponding angles $2\theta = 26$, 29.70, 30.20 and 35.80.

The first phase indexes as $Ba_3Si_5O_{13}$, the second as Ba_3SiO_4 and the third phase as a result of $Ba_2Cu_3O_5$ (ASTM cards) presence, which means that the first and second phases are due to barium silicate, but with different composition, and the third phase is barium cuprate. The 1–2–3 phase is still present with Si = 0.5 and 1% doping, but decreases with a correlated increase of barium silicate and barium cuprate phases. At Si = 2% doping, the strongest peak (1 0 3) of the orthorhombic 1–2–3 phase is greatly decreased and the barium silicate, barium cuprate phases are very clearly demonate and destroying the superconducting 1–2–3 phase. At the final step, Si = 5% doping, the 1–2–3 has completely disappeared and only the characteristic peaks of barium silicate and barium cuprate exist.

4. Discussion

The difficulties in fabricating high quality Y–Ba–Cu–O 'Superconductor' with Si 'Semiconductor' arise from many factors.

4.1 Chemical reactions between Y–Ba–Cu–O and Si

These reactions lead to the formation of barium silicate, barium cuprate and the decomposition of an orthorhombic 1–2–3 phase which reduce T_c with small Si doping and finally lead to complete decomposition with large Si doping (Si $\geqslant$ 2%).

4.2. Replacement of Cu sites by Si

The substitution of the Cu ions in the 1–2–3 phase (replacement of Cu ions by dopant ions) can indeed have a dramatic effect on T_c [5–9]. Interpretation of this doping is difficult, however, as dopant ions could substitute on the Cu^{2+} site, Cu^{3+} site or both sites depending upon the radius, charge and electronic configuration of dopant ions. Strongly charged ions such as Si^{4+} are reluctant to substitute for Cu ions, but it was also reported that samples prepared with a nominal 7% of Cu replaced by Si still have superconductivity with $T_c = 85$ K [10].

A model for correlated valence fluctuation of Cu^{3+} and Cu^{2+} proposed by W. Y. Liang [11] will be employed to discuss our results. In this model, electron pairs are formed by coulomb interaction between electrons, mainly Cu^{2+} pyramidal planes mediated by Cu^{3+} ions in the CuO chain-like plane in $Y_1Ba_2Cu_3O_{7-\delta}$. These electron pairs have high binding energies necessary for high-T_c superconductivity. The electrons in the middle plane Cu^{3+} do not form pairs and therefore are likely to remain 'normal electrons' over all the temperature ranges, thus the Cu^{3+}/Cu^{2+} ratio plays a very important role in HT_c Y–Ba–Cu–O superconductors, because T_c is very sensitive to this ratio and increases with it [12–14].

The results of d.c. resistance, a.c. magnetic susceptibility and XRD of 1–2–3 superconductor doped with Si can be explained as follows.

(i) For samples with Si $\leqslant 1\%$, the decrease in T_c may be attributed to the introduction of Si^{4+}, which causes a very slight disturbance that finally smoothly decreases with Cu^{3+}/Cu^{2+} ratio, which tends to decrease T_c. From X-ray results, it is concluded that the existence of a barium silicate phase will produce a decrease in the 1–2–3 phase, a new Si compound phase whose superconducting transition $T_c = 135$ K is formed. Evidence in support of this assumption is the semiconducting nature of $R(T)$ curve around this drop in resistance. This drop in resistance at $T_c = 135$ K may be due to the existence of holes as Si^{4+} partially replaces Cu^{3+}, beside normal electrons, resulting in a drop in resistance. This drop in $R(T)$ curve with new $T_c = 135$ K phase is also attributed to the presence of electron pairs persisting above base condensation temperature.

(ii) By increasing the Si ratio (Si $\geqslant 2\%$) the ratio Cu^{3+}/Cu^{2+} becomes so small and the probability of formation electron pairs is reduced to an extent that it degrades the superconducting phase. As concluded from X-ray results, the 1–2–3 phase is extensively decreased and the barium cuprate, barium silicate phases are increased and decomposed the superconducting phase.

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