Effect of Rb and Cs doping on superconducting properties of MgB$_2$ thin films

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Abstract

A Rutherford backscattering spectrometry (RBS) study has found that concentrations up to 7 at.% of Rb and Cs can be introduced to a depth of $\sim 700 \, \text{Å}$ in MgB$_2$ thin films by annealing in quartz ampoules containing the elemental alkali metals at $< 350 \, ^\circ\text{C}$. No significant change in transition temperature ($T_c$) (determined resistively) was observed, in contrast to an earlier report of very high $T_c$s ($> 50 \, ^\circ\text{K}$) from susceptibility measurements on MgB$_2$ powders. The lack of a significant change in $T_c$ and intra-granular carrier scattering suggests that Rb and Cs diffuse into the film, but do not enter the grains. Instead, the observed changes in the electrical properties, including a significant drop in $J_c$ and an increase in $\Delta \rho (\rho_{300} - \rho_{40})$, arise from a decrease in inter-granular connectivity due to segregation of the heavy alkaline metals and other impurities (i.e. C and O) introduced into the grain boundary regions during the anneals.

1. Introduction

A recent report [1], as yet unpublished, of very high ($> 50 \, ^\circ\text{K}$) onsets of superconductivity in Rb- and Cs-doped MgB$_2$ has caused other researchers to study the effect of heavier alkali metals on MgB$_2$ superconducting properties. According to Palnichenko et al [1], the very electropositive heavier alkali and alkaline earth metals can donate carriers to the electron system, thereby enhancing the superconducting properties of the host MgB$_2$ material. A significantly enhanced $T_c$ was reported in susceptibility measurements of bulk samples made by treating MgB$_2$ powder and granules with Rb, Cs and Ba through a liquid phase reaction. The concentration and spatial distribution of the dopants were not reported in that work.

In the study reported here, we have studied the effect of Cs and Rb on MgB$_2$ electrical properties by diffusing them into thin films grown by MBE (molecular beam epitaxy). A quantitative determination of the dopant concentration has also been made using Rutherford backscattering spectrometry (RBS).

2. Experimental details

MgB$_2$ films of thicknesses 1400–2200 Å were deposited on (0001) sapphire at either room temperature ($\sim 25 \, ^\circ\text{C}$) or 300 ± 2 °C in an ultra-high vacuum MBE system with a typical unbaked pressure of $\sim 7 \times 10^{-9}$ Torr. The system pressure reached as high as $10^{-6}$ Torr during deposition. Further growth details have been published elsewhere [2, 3]. The thickness and the depth profile of the chemical composition were determined using Rutherford backscattering spectrometry. Nuclear resonant elastic scattering, $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ and $^{12}\text{C}(\alpha, \alpha)^{12}\text{C}$ was used for oxygen and carbon detection, respectively. This technique can detect up to 0.5% of impurity with an accuracy greater than 95%. The areal atomic density is directly determined by RBS and then a thickness can be inferred using the known material density. Some films were patterned into a 100 $\mu$m $\times$ 1 mm bridge using photolithography and reactive ion etching (Ar plasma) to provide for four-point contact measurements of resistivity and critical current density ($J_c$).

In an inert atmosphere glove box, these films were loaded into rigorously clean clear fused quartz ampoules with an elemental Mg chip and approximately 0.5 cm$^3$ of alkali metal (Rb or Cs). The films were kept away from the metals by means of individual quartz containers within the ampoule separated by a quartz spacer. The ampoule with contents was then transferred to a vacuum manifold and evacuated to $5 \times 10^{-5}$ Torr and sealed using a hydrogen/oxygen torch. A quartz handle was attached to allow for control of the ampoule while in the vertical three-zone clamshell tube furnace used to anneal...
the ampoule and during quenching. Annealing was done over a wide temperature range (100–350 °C) and time (12–100 h). At the time of quenching, the metal end of the ampoule was lowered into ice water before the region containing the thin film, so that metal vapor condensed on the colder end of the ampoule instead of on the thin film. Four-terminal current–voltage measurements were made using either a Quantum Design physical property measurement system (PPMS) or a custom-built dipping probe using direct contacts in unpatterned films and silver contacts in patterned films.

### 3. Results and discussion

#### 3.1. Chemical composition of annealed films

Table 1 summarizes the annealing treatment and post-annealed composition of the MgB$_2$ films. One sample (X-1) was annealed without any dopant to distinguish the contribution of the post-growth thermal treatments from doping-induced changes in the MgB$_2$ superconducting properties. We observe an inhomogeneous distribution of Rb or Cs with depth in all the samples studied. The greatest concentration of Rb doping (7 at.% in the top 700 Å layer and 4.3 at.% in the bottom 700 Å layer) was achieved in the film Rb-4 after a thermal treatment of 350 °C for 15 h followed by water quenching the ampoule. When a similar thermal treatment was given to a MgB$_2$ film grown at room temperature (Rb-3), considerably lower (<1 at.%) Rb content was observed in the film. In the case of Cs, a maximum surface doping (4.7 at.%) and sub-surface doping (0.8 at.%) was achieved after thermal treatments at 160 °C for 20 h followed by 100 °C for 100 h (Cs-3) and 200 °C for 18 h (Cs-1), respectively. In some samples, we also observe changes in film thickness after thermal treatment. This increase in thickness is presumably a result of the reaction of the film with the ambient atmosphere or the ampoule. However, the reason for the reduction in the areal density and the inferred thickness in the sample annealed at 300 °C (Cs-2) is not clear. The vapor pressure of thin films of MgB$_2$ at this temperature has been shown to be very small ($\ll 10^{-7}$ ML s$^{-1}$) [4].

We observe clear evidence of Cs diffusing into the substrate after all thermal treatments (160–300 °C). However, diffusion of Rb into the substrate is seen only at temperatures above 200 °C. In the Rb-doped sample annealed at 200 °C (Rb-1), Rb could not be detected in the bottom 400 Å of the film. Figure 1 shows RBS analysis of the Cs-doped sample with a high level of oxygen contamination in the MgB$_2$ film, in conjunction with a significant amount of Cs that has diffused into the sapphire substrate.

A significant oxygen and carbon contamination is consistently observed in the films containing large Cs and Rb doping concentrations (table 1). The increase in carbon and oxygen generally scales in direct proportion to the Rb and Cs content. In the film with the highest reported doping level of ~7 at.% Rb (Rb-4) oxygen content increased from ~5 at.% to ~35 at.% and carbon content increased from <0.5 at.% to ~15 at.% after the doping process. Similarly, in the film with ~2.7 at.% Cs doping level (Cs-1), oxygen content increased from ~0.55 at.% to ~22 at.% and carbon content increased from <0.5 at.% to ~8 at.% after the doping process. There are, however, two exceptions to this—the room temperature grown film has a relatively higher level of contamination and the Cs-doped film annealed at low temperatures (160 °C, 20 h + 100 °C, 100 h) has a relatively lower contamination. We believe that the contamination is introduced after the samples are taken out from the ampoules for electrical measurements.

### Table 1. Chemical composition of MgB$_2$ films before and after thermal treatment.

| #   | Thermal treatment | Composition and thickness before treatment | Composition and thickness after treatment |
|-----|-------------------|--------------------------------------------|------------------------------------------|
| X-1 | 300 °C/15 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.3}$ (1450 Å) | Mg$_{1.05}$B$_2$O$_{0.3}$ (1470 Å) |
| Rb-1 | 200 °C/12 h, air cooled | Mg$_{1.05}$B$_2$O$_{0.04}$ (2150 Å) | Mg$_{1.05}$B$_2$O$_{0.04}$ (middle 1500 Å) |
| Rb-2 | 300 °C/15 h, water quenched + air annealed 200 °C/7 h | Mg$_{1.05}$B$_2$O$_{0.3}$ (1700 Å) | Mg$_{1.05}$B$_2$O$_{0.3}$ (top 800 Å) |
| Rb-3b | 350 °C/15 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.05}$ (1700 Å) | Mg$_{1.05}$B$_2$O$_{0.05}$ (750 Å) |
| Rb-4 | 350 °C/15 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.15}$ (1400 Å) | Mg$_{1.05}$B$_2$O$_{0.15}$ (bottom 700 Å) |
| Cs-1 | 200 °C/18 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.05}$ (1400 Å) | Mg$_{1.05}$B$_2$O$_{0.05}$ (top 60 Å) |
| Cs-2 | 300 °C/18 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.05}$ (1400 Å) | Mg$_{1.05}$B$_2$O$_{0.05}$ (1100 Å) |
| Cs-3 | 160 °C/20 h + 100 °C/100 h, water quenched | Mg$_{1.05}$B$_2$O$_{0.15}$ (3200 Å) | Mg$_{1.05}$B$_2$O$_{0.15}$ (2200 Å) |

* Sample annealed without dopant.
* Sample grown with substrate at room temperature.
3.2. Effect of dopants on superconducting properties

Table 2 summarizes the effect of Rb/Cs incorporation on the critical temperature \(T_c\), resistivity \(\rho_{300 \, K}\), \(\rho_{40 \, K}\), \(\Delta \rho\) and \(\rho_{40 \, K, \text{corrected}}\), critical current density \(J_c\) and upper critical field slope \((dH_c2/dT)_{T_c}\) of MgB\(_2\) films. Critical current density \(J_c\) measurements were only performed on selected films that could be patterned into 100 \(\mu\)m \(\times\) 1 mm bridges. Properties that could not be measured as a result of the rapid degradation of the films, presumably as a result of exposure and subsequent reaction with the air, are left blank in the table.

Table 2. Effect of Rb or Cs incorporation on the critical temperature, resistivity, critical current density and upper critical field slope of MgB\(_2\) thin films.

| #    | Condition   | \(T_c\) (K) | \(\rho_{300 \, K}\) (\(\mu\Omega\) cm) | \(\rho_{40 \, K}\) (\(\mu\Omega\) cm) | \(\Delta \rho\) (\(\mu\Omega\) cm) | \(\rho_{40 \, K, \text{corrected}}\) (\(\mu\Omega\) cm) | \(J_c @ 10 \, K\) (A cm\(^{-2}\)) | \((dH_c2/dT)_{T_c}\) (T K\(^{-1}\)) |
|------|-------------|--------------|-------------------------------------|-----------------------------------|-------------------|---------------------------------|----------------------------------|---------------------------------|
| X-1  | As-grown    | 32.8         | 31.2                                | 98                                | 75                | 23                             | 24                               | 1.6 \(\times\) 10\(^3\)         | 1.3                             |
|      | Annealed    | 34.5         | 30.8                                | 680                               | 570               | 120                            | 35                               | 1.6 \(\times\) 10\(^3\)         | 1.2                             |
|      |             | 34.9         | 31.4                                | 41                                | 26                | 15                             | 13                               | —                               | —                               |
| Rb-1 | As-grown    | 34.1         | 32.8                                | 120                               | 88                | 27                             | 24                               | 1.7 \(\times\) 10\(^6\)         | 1.1                             |
|      | Annealed    | 35.0         | 32.6                                | 250                               | 230               | 20                             | 84                               | 6.8 \(\times\) 10\(^4\)         | 1.2                             |
| Rb-2 | As-grown    | —            | —                                   | —                                 | —                 | —                              | —                                | —                               | —                               |
|      | Annealed    | —            | —                                   | —                                 | —                 | —                              | —                                | —                               | —                               |
| Rb-3 | As-grown    | 32.8         | 31.2                                | 98                                | 75                | 23                             | 24                               | 1.1 \(\times\) 10\(^6\)         | 1.2                             |
|      | Annealed    | 34.5         | 30.1                                | 680                               | 560               | 120                            | 35                               | 5.8 \(\times\) 10\(^3\)         | 1.2                             |
| Cs-1 | As-grown    | —            | —                                   | —                                 | —                 | —                              | —                                | —                               | —                               |
|      | Annealed    | 34.3         | 33.3                                | 170                               | 130               | 37                             | 26                               | —                               | 0.9                             |
| Cs-2 | As-grown    | —            | —                                   | —                                 | —                 | —                              | —                                | —                               | —                               |
|      | Annealed    | 34.7         | 33.7                                | 300                               | 250               | 58                             | 31                               | —                               | 1.0                             |
| Cs-3 | As-grown    | 35.4         | 33.8                                | 150                               | 110               | 37                             | 22                               | —                               | 0.9                             |
|      | Annealed    | 35.8         | 34.6                                | 180                               | 130               | 46                             | 22                               | —                               | 0.9                             |

3.2.1. Effect on transition temperature. For both Rb and Cs doping, we see a small, but measurable, change (\(<\)2 K) in the transition temperature. A similar change is also observed in the sample that was annealed without dopants. It is evident, therefore, that the observed changes are a result of thermal treatment and not necessarily a direct consequence of the presence of Rb or Cs in the film.

It is interesting to note that the width of the transition appears to decrease slightly after introducing Cs (from \(\Delta T_c = 1.4 \pm 0.2\) to \(1.1 \pm 0.1\) K), while it increases significantly during the thermal processing in the absence of a dopant and when Rb was introduced (to \(\Delta T_c = 3.1 \pm 0.6\) K).

3.2.2. Effect on resistivity. We observe a large increase (\(\geq 100\%\)) in the resistivity at 300 K (\(\rho_{300}\)) and 40 K (\(\rho_{40}\)) in all the samples, including the annealed undoped sample. This indicates that the increased resistivity arises primarily from the thermal treatment and is not necessarily related to the presence of Rb or Cs in the film. The increase in resistivity is relatively small (20%) in the sample that was annealed with Cs at 160 °C for 20 h followed by 100 °C for 100 h. This is presumably a consequence of being exposed to the relatively low annealing temperatures in this case.

We also observe an increase in \(\Delta \rho\) (\(\rho_{300} - \rho_{40}\)) in post-annealed films, except in the Rb-2 sample, where a marginal drop in \(\Delta \rho\) is observed. \(\Delta \rho\), as pointed out by Rowell [5], is a measure of the inter-grain connectivity in MgB\(_2\) samples. An increase in \(\Delta \rho\) reflects a decrease in the connectivity, presumably as a result of oxidation or other forms of contamination segregating to the grain boundaries. If we compare changes in \(\Delta \rho\) (table 2) with the extent of impurity contamination that occurs during annealing (table 1), we see that Rb-2 is the only sample where the oxygen and carbon concentrations did not change after annealing. This sample shows a drop in \(\Delta \rho\) after annealing. In all other samples, we see a large increase in oxygen and carbon content after annealing that is strongly correlated with the large increase in \(\Delta \rho\). It appears, therefore, that oxygen and carbon incorporation into the film contaminates grain boundaries and...
thus reduces inter-grain connectivity. The change in inter-grain connectivity is found to scale proportionately with oxygen and carbon concentration. The largest change found for $\Delta \rho$ is a factor of 5 (Rb-4) and this is accompanied with an increase in the impurity content from 5 at.% to 40 $\pm$ 10 at.% (50% in the top layer and 30% in the bottom layer).

The residual resistivity ($\rho_{40 \, K}$) can be corrected to obtain intra-grain resistivity values using the Rowell analysis [5]. This procedure is invoked to isolate the influence of intra-grain resistivity from the inter-grain connectivity in the electrical properties. Rb-2, which shows improved inter-grain connectivity, also shows the largest increase in intra-grain resistivity after thermal treatment. This could be due to increased carrier scattering by Rb or an Rb-containing phase present within the grain. Palnichenko et al. [1] have reported the presence of a phase with a cubic symmetry and charge accumulation at the boron site in the Rb-doped samples. Since other samples do not show a large increase in carrier scattering, it is possible that, in these samples, dopants (Rb/Cs) are mostly present at grain boundaries and only a small fraction of dopant is present within the grain.

3.2.3. Effect on critical current and slope of upper critical field. After thermal treatment, we observe a significant drop in critical current density (table 2), presumably from a decrease in connectivity. At this point, we are not certain if this drop is due to annealing or the presence of Rb or Cs in the sample. We also note that doping and/or thermal treatment does not have a measurable effect on the slope of the upper critical field $[\frac{dH_c}{dT}]_{T_c}$, again suggesting that the dopants have no effect on the superconducting properties of the MgB$_2$ grains.

Our results show that the Rowell analysis is useful in identifying the influence of the inter-granular connectivity and intra-granular resistivity on the electrical properties, and they also might suggest some limitations. For example, the $\rho_{40 \, K}$ can be corrected by a factor that represents the aerial current-carrying fraction ($\gamma = \rho_{40 \, K}/\rho_{40 \, K, ideal} \approx \rho_{40 \, K}/7.4 \, \mu\Omega \cdot \text{cm}$) [6, 7] to obtain a $\rho_{40 \, K, corrected}$ that is characteristic of the intra-granular resistivity alone. Measurements of $T_c$ and the corrected value of the residual resistivity of MgB$_2$, after both ion and neutron irradiation [6, 8], suggest a universal linear dependence, with $T_c$ extrapolating to 0 K for $\rho_{40 \, K, corrected}$ values of $\sim 90 \, \mu\Omega \cdot \text{cm}$. Although it is clear that the Rowell analysis is correcting in the right direction, our results suggest that the accuracy of the analysis might be limited when there are very large deviations from the MgB$_2$ chemical composition, possibly resulting from the annealing process and potential reaction of magnesium and/or boron with other chemical species (i.e. Rb/Cs). This is not surprising. We base our conclusion on the fact that the values of $T_c$, for the corrected values of $\rho_{40 \, K}$, are higher than would be expected for the universal dependence. Furthermore, the $J_c$ is found to vary by a factor of over 25 and yet the connectivity only changes by a factor of $\sim 6$.

4. Conclusion

Rb and Cs with concentrations ranging from 0 to 7 at.% have been incorporated into MgB$_2$ thin films by annealing at temperatures up to 350 $^\circ$C with elemental alkali metals in an evacuated and then sealed quartz ampoule. In contrast to the as yet unpublished report for bulk MgB$_2$ doped with heavy alkali and alkaline earth metals [1], we did not find evidence for enhanced transition temperatures (>50 K) in either Rb- or Cs-doped MBE grown thin films. The $T_c$ and $\frac{dH_c}{dT}$ of thin films remain unaffected by doping. The earlier study of Palnichenko et al. [1] presented a small, but measurable, drop in the magnetic susceptibility of powders and granules as evidence for superconductivity. In the present study, we have measured superconductivity in thin films using four-point contact resistivity measurements. The increase in the level of oxygen and carbon contamination after the doping treatment can be related to the unusually high reactivity of Rb and Cs. The resulting presence of impurities at the grain boundaries leads to an increase in resistivity and drop in $J_c$ of the doped films.

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