Superconducting properties of MgB$_2$ thin films prepared on flexible plastic substrates

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Superconducting MgB$_2$ thin films were prepared on 50-$\mu$m-thick, flexible polyamide Kapton-E foils by vacuum co-deposition of Mg and B precursors with nominal thickness of about 100 nm and a subsequent ex situ rapid annealing process in an Ar or vacuum atmosphere. In the optimal annealing process, the Mg–B films were heated to approximately 600 °C, but, at the same time, the backside of the structures was attached to a water-cooled radiator to avoid overheating of the plastic substrate. The resulting MgB$_2$ films were amorphous with the onset of the superconducting transition at $T_c\approx 29$ K and a transition width of approximately 3 K. The critical current density was $>7 \times 10^5$ A/cm$^2$ at 4.2 K, and its temperature dependence indicated a granular film composition with a network of intergranular weak links. The films could be deposited on large-area foils (up to 400 cm$^2$) and, after processing, cut into any shape (e.g., strips) with scissors, or bent multiple times, without any observed degradation of their superconducting properties. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507828]

The recent discovery of superconductivity at 39 K in hexagonal magnesium diborides$^1$ has stimulated very intensive investigations of the fundamental mechanism of superconductivity in MgB$_2$, as well as the possible practical applications. In comparison with high-temperature cuprates, MgB$_2$ superconductors have more than two times lower anisotropy, significantly larger coherence length, and higher transparency of grain boundaries to the current flow. At the same time, when compared to conventional metallic superconductors (including Nb$_3$Sn or NbN), they have at least two times higher critical temperature $T_c$ and energy gap, as well as higher critical current density $j_c$. As a result, MgB$_2$ superconductors are expected to play an important role for high-current, high-field applications, as well as in cryoelectronics, where they might be the material of choice for above 300 GHz clock-rate digital electronics. In addition, MgB$_2$ devices could operate in simple cryocoolers.

The availability of high-quality superconducting thin films with single-crystal-like transport properties$^2$ is the key to realization of practical MgB$_2$ cryoelectronic devices. The films with high values of $T_c$ and $j_c$ have been prepared on SrTiO$_3$, Al$_2$O$_3$, Si, SiC, and other substrates by various deposition techniques.$^3$–$^8$ All of the above procedures required postannealing at temperatures higher than 600 °C, and the superconducting properties of the resulting films depended very strongly on the conditions of their annealing. The best reported MgB$_2$ thin films are characterized by $T_c\approx 39$ K and $j_c>10^7$ A/cm$^2$ at 4.2 K and $5 \times 10^5$ A/cm$^2$ at 30 K, both at the zero external magnetic field.$^9$ Preparation of MgB$_2$ thin films on unconventional substrates, such as stainless steel$^{10}$ or plastic foils, is also desirable. MgB$_2$-on-steel films are interesting for the preparation of low-magnetic shielding and antennas, while plastic foils are very attractive for their bending and shaping abilities.

In this letter, we present the preparation and superconducting properties of MgB$_2$ thin films fabricated on flexible substrates (Kapton-E polyamide foil), using three specially designed, rapid annealing processes. Flexible plastic substrates introduce a number of aspects to superconducting technology, such as the ability to cut the final structures into desired shapes for, e.g., magnetic shielding. They are also unbreakable and can be rolled into small superconducting coils or form flexible microwave or high-speed digital microstrips and coplanar transmission lines.

Kapton-E foils up to $20 \times 20$ cm$^2$ (limited in size by our deposition apparatus) were cleaned in acetone, ultrasonically washed in ethanol, and air dried before being placed in our vacuum chamber. Mg–B precursor films 100–200 nm thick with a nominal composition of 1:2 were prepared on the unheated foil by simultaneous evaporation of Mg (purity 99.8%) and B (purity 99.9%) from separate W and Ta resistive heaters at a vacuum of $8 \times 10^{-4}$ Pa.$^7$ After deposition, the Mg–B films were ex situ annealed in a special low-temperature process to avoid overheating the Kapton foil, which had to be kept below its 300 °C deformation temperature.

Several rapid annealing procedures have been implemented. Initially, the Mg–B films were placed inside a quartz
tube on a thick sapphire plate and introduced for 10–300 s into a preheated furnace. The furnace temperature varied from 350° to 500°C, and the Ar atmosphere could be changed from 3 to 100 kPa in a flow regime. In another approach, the Mg–B films were placed “face down” on a resistive heater and annealed at 500–600°C in pure Ar for 60–180 s. For overheating protection, the foil was covered with a sapphire plate and a large Cu block on top. After annealing, the samples were cooled down in approximately 30 s to room temperature. Both of the above annealing methods resulted in superconducting MgB2 with $T_{c, on}$ up to 33 K and a transition temperature $\Delta T_c \approx 10$ K. The highest $T_{c, on}$ was obtained after annealing for 180 s at 500°C on a resistive heater. Unfortunately, under such conditions, the color of the Kapton foil changed from yellow to black and it partially lost its flexibility. The maximal $j_c$ was only about 500 A/cm² at 4.2 K, suggesting that the damaged foil stressed the MgB2 film.

Much better results were obtained using the third annealing method; thus, the remainder of this work will be devoted to those films. The Mg–B thin films were radiatively heated with halogen lamps in vacuum; simultaneously, the substrate side of our samples was placed on an external water-cooled radiator to protect the plastic foil. The distance between the samples and the halogen source was 7 cm, and the vacuum chamber was pumped down to a base pressure of $1 \times 10^{-2}$ Pa to minimize the oxygen content and other gas impurities during annealing. The foil temperature was controlled by a thermocouple located very close to its Mg–B surface. The duration of the annealing process was 60–180 s, and the temperature at the film surface varied from 300 to 650°C. After annealing, the vacuum chamber was filled with Ar and the films were cooled to room temperature in 20–30 s. Even for the highest Mg–B annealing temperature, the Kapton was always kept below 300°C, no deformation or change of color was observed, and the resulting MgB2 samples were fully flexible.

Figure 1 shows the surfaces and the critical temperature parameters of three films annealed under different conditions. For samples annealed for at least 1 min at film surface temperatures of 550–650°C, the MgB2 morphology exhibited domains or lamellar structures (Figs. 1(a) and 1(b), respectively) and their maximal $T_{c, on}$ was only 20 and 30 K, respectively. The film presented in Fig. 1(b) showed signs of heat-induced substrate damage and its $\Delta T_c$ was very wide. After extensive trial-and-error studies, we realized that the best annealing conditions consisted of preheating at 300°C and only very brief, 30 s heating at 600°C, followed by postheating for 60 s again at 300°C. The films produced in this manner were characterized by very smooth surfaces (Fig. 1(c)), without domains, cracks, or lamellar structures. X-ray diffraction exhibited no diffraction peaks, indicating an amorphous phase, in analogy to our earlier obtained MgB2 films, prepared on Si and sapphire substrates from Mg–B precursors.

The homogeneity of our thin films was studied by Auger spectroscopy. The Auger spectra (Fig. 2) show a strong non-stoichiometry of Mg and B on the film surface, as well as an enhanced content of oxygen and presence of carbon. However, the damaged surface layer was only ~20 nm thick, as estimated by the rate of Mg–B etching and scanning electron microscopy studies. The bulk of the film had a uniform 1:2 stoichiometry ratio, with only small oxygen content, apparently from the residual oxygen in the annealing vacuum chamber.

The films prepared according to the annealing recipe shown in Fig. 1(c) also had the best superconducting properties. The maximum $T_{c, on}$ obtained was 29.3 K, as shown in Fig. 3, where we plotted the resistive superconducting transitions for both the strip cut from a film by scissors and the one patterned by photolithography and Ar-ion etching. The cut strip was approximately 1 mm wide and its superconducting properties were representative for our plain MgB2 films. The strips cut from the same MgB2-coated foil exhibited exactly the same normal-state and superconducting electrical properties. On many occasions, prior to performing resistive measurements, we repeatedly bent our strips on a 5-mm-diam glass rod, twisted them, and/or rolled them into a solenoid form. The above procedures did not affect our films and their electrical properties remained unchanged. We have not completed long-term aging studies, but our films warmed up to room temperature after liquid-helium testing, always...
regained their full flexibility and, in repeated tests, we did not see any degradation of their superconducting properties.

The photolithographically patterned bridges were typically 10 μm wide and 120 μm long. We note in Fig. 3 that Ar-ion etching resulted in a slight reduction of $T_{c,\text{on}}$; at the same time, however, $\Delta T_c$ decreased to 2 K. The patterned microbridges were also used for $j_c$ measurements. The inset in Fig. 3 shows the $j_c$ dependence on temperature, together with the fit based on the $j_c(T) = k(1 - T/T_c)^\alpha$ expression, where $k$ is a constant and $\alpha$ is a fitting parameter. The fit shown in Fig. 3 was obtained for $\alpha = 2$ and indicates that our films are granular with a network of superconductor-normal metal-superconductor (SNS) weak links. 11 At 4.2 K, $j_c$ reached a value $\gtrsim 7 \times 10^5$ A/cm².

In conclusion, the preparation of superconducting MgB₂ thin films on flexible plastic foils has been presented. Our films were amorphous and exhibited very smooth surfaces. Annealing under optimal conditions, using rapid radiative (halogen lamps) heating of Mg–B and simultaneous water cooling of the Kapton foil, resulted in fully flexible films. The films were stable upon moderate stress and repeated thermal cycling, and their superconducting properties were characterized by $T_{c,\text{on}}$ of about 29 K, $\Delta T_c$ of about 3 K, and $j_c \gtrsim 7 \times 10^5$ A/cm² at 4.2 K. The measured $j_c(T)$ characteristics indicated the presence of a SNS weak-link network in the films. The Auger measurement showed that besides the ~20-nm-thick film surface, the bulk of the film exhibited a fully stoichiometric composition of Mg and B. Finally, we note that our rapid annealing procedure prevented any substrate degradation and is suitable for high-temperature annealing thin films prepared on substrates unstable at high temperatures.

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