Chemical Vapor Deposition of the Superconductor YBa$_2$Cu$_3$O$_{7-x}$(s) from the Gas Phase

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The deposition of the condensed phase YBa$_2$Cu$_3$O$_{7-x}$ from a gas mixture composed of YCl$_3$, BaCl$_2$, Cu$_3$Cl$_3$, and Ar reacting with another consisting of O$_2$ and Ar in a flow system at elevated temperatures was investigated by means of the virtual equilibrium model, and the deposition rates were computed as a function of input gas stream compositions. The optimum growth conditions were identified.

KEY WORDS: Chemical vapor deposition; YBa$_2$Cu$_3$O$_{7-x}$

1. INTRODUCTION

The oxygen-deficient perovskite compounds such as YBa$_2$Cu$_3$O$_{7-x}$ with high $T_c$ superconductivity are currently the subject of most intense scrutiny by a number of investigators worldwide. The conventional method for preparing the yttrium barium copper oxide superconductor involves sintering an appropriate mixture of Y$_2$O$_3$, BaCO$_3$, and CuO fines at about 900°C under air or oxygen. The ceramic compound oxide thus prepared is usually porous and brittle; and it is not amenable to further processing into desired shapes. At present, there is a practical need for the fabrication of high-temperature superconductors into fine fibers or film-coated composite wires which can be wound into a solenoid configuration.

Thin Y-Ba-Cu-O films were grown on MgO substrates by dc magnetron sputtering using a sintered stoichiometric YBa$_2$Cu$_3$O$_{7-x}$ compound as target; deposition was carried out at about 100°C with a pure argon atmosphere (3–40 mTorr) in the sputtering chamber, and a deposition rate of

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150 Å · min⁻¹ was obtained [1]. It is known that substitution of certain rare-earth (La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu) atoms in place of Y in the 1:2:3 oxide compound does not adversely affect the superconducting properties [2,3]. The deposition of thin films of DyBa₂Cu₃O₇₋ₓ using molecular beam epitaxy (MBE) was investigated by Webb and co-workers [4]. Beams of dysprosium, barium, and copper atoms produced by separate furnaces were directed toward a SrTiO₃ substrate heated to 600-750°C. The oxygen pressure was at about 7 × 10⁻⁶ Torr with the growth rate approximating 0.64 Å · s⁻¹. Oh et al. [5] describe the preparation of thin films of YBa₂Cu₃O₇₋ₓ using electron-beam coevaporation of Y, Ba, and Cu metals; with an oxygen pressure of about 5 × 10⁻⁶ Torr, growth rates of 10 Å · s⁻¹ were observed.

Dense wires and spun ribbons of YBa₂Cu₃O₇₋ₓ were prepared from melts of appropriate composition by Jin and co-workers [6]. Composite superconducting wires with a metal (Ag) core coated with the ceramic YBa₂Cu₃O₇₋ₓ oxide was also produced by these authors. Thin films (2000 Å thick) of superconducting YBa₂Cu₃O₇₋ₓ were made by spin coating the substrate (MgO) with a solution of a stoichiometric mixture of the metal acetates followed by pyrolysis in air at about 400°C and then a high-temperature heat treatment in oxygen at 980-990°C [7]. The metal organic deposition (MOD) technique was used by Hamdi et al. [8] to produce superconducting thin film on single crystal (100) SrTiO₃. A spin coat of a liquid solution of neodecanoates of copper, barium, and yttrium was formed on the substrate; the organic film was then treated in air or oxygen to burn off the organics, leaving behind a film of the superconducting oxide YBa₂Cu₃O₇₋ₓ. Tsaur, Dilorio, and Strauss [9] describe a novel method for producing thin films of yttrium barium copper oxide superconductor. A multilayer metal film was deposited on a sapphire (Al₂O₃) substrate by sequential electron beam evaporation of Cu, Ba, and Y. The film was then annealed and homogenized in a stream of oxygen at 800-850°C for a duration of 0.5-4 h, resulting in a single-phase specimen (3500-7100 Å thick) of YBa₂Cu₃O₇₋ₓ on the substrate.

The phase equilibria in the Y-Ba-Cu-O system were investigated by Roth et al. [10]. The superconducting phase YBa₂Cu₃O₇₋ₓ melts incongruently at about 1010°C, producing Y₂BaCuO₅ (green phase) and a liquid. The oxygen-deficiency (x) of YBa₂Cu₃O₇₋ₓ is strongly dependent upon temperature and oxygen potential of the gas phase. The extensive thermoanalytical measurements of Gallagher [11] show that the compound oxide reaches the lowest oxidation state (x = 1.0) at about 950°C in an atmosphere containing 10⁻³ atm. O₂; the highest oxidation state (x = 0.0), virtually independent of O₂ pressure, is approached at a temperature of about 400°C. The superconductor YBa₂Cu₃O₇₋ₓ undergoes an orthorhombic → tetragonal