JOURNAL OF MATERIALS SCIENCE 26 (1991) 2967–2970

Deposition of superconductive thin films by laser PVD

A. ROTH*, M. RIABKINA-FISHMAN‡, J. ZAHAVI‡, A. ROSEN*
*Department of Materials Engineering, and ‡Israel Institute of Metals, Technion, Israeli Institute of Technology, Haifa, Israel

Thin films of the superconductive $YBa_2 Cu_3O_{7-k}$ have been deposited on $SrTiO_3$ substrates by means of a pulse laser ablation technique, with variable substrate temperature, number of pulses and repetition rate of the laser beam. High substrate temperatures and low rates of repetition resulted in good quality superconducting films.

1. Introduction

Since the discovery of the superconductive behaviour of $YBa_2Cu_3O_{7-k}$ (YBCO) [1] compound at high temperatures it has been realized that there are certain advantages in preparing thin films of this compound by methods which do not require high-temperature (> 800 °C) heat treatments [2, 3]. One of the techniques for the *in situ* preparation of high T_c thin films is that of pulse laser deposition [4–7]. This technique has many advantages such as good control of stoichiometry [4] and other parameters which affect the quality of the film. The YBCO compound has anisotropic electrical properties, i.e. electrical conductivity is much better on the Cu–O planes of the unit cell [8]. By this method it is possible to grow superconductive thin films with preferred orientation, in order to align the Cu–O planes of the unit cell parallel to the surface of the substrate.

The aim of the investigation presented in this paper, was the deposition of YBCO films on strontium titanate (1 0 0) substrates by means of ArF excimer laser. There are many variables which influence the quality of the films, the major ones being the substrate temperature and the laser repetition rate. These variables are known to influence the crystalline structure of the film, namely whether it grows as amorphous, polycrystalline or single crystal [9]. These parameters and others were studied in order to achieve optimal conditions for growing the best quality films.

The films were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and electrical measurements at various temperatures.

2. Experimental procedure

The experimental apparatus is shown in Fig. 1. It consists of a stainless steel vacuum chamber, a rotating target and the substrate holder. The laser beam was produced by an ArF pulsed excimer laser (Lambda Physik EMG 201) having a wavelength of 193 nm and pulse duration of 24 ns.

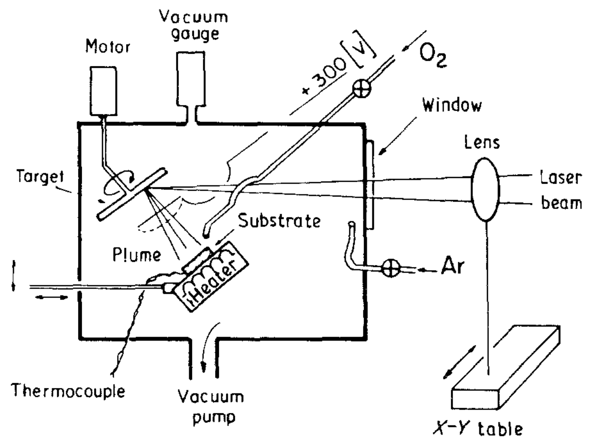

Figure 1 Schematic illustration of the experimental apparatus.

A typical experiment was carried out as follows. A ceramic target pellet of YBCO composition was prepared by conventional powder sintering. The X-ray diffraction pattern (XRD) of a typical pellet is shown in Fig. 2, in which $YBa_2\ Cu_3O_{7-k}$ polycrystalline peaks can be seen. The target was placed on a holder which was rotated at 12 r.p.m. The cell was evacuated to a base pressure of approximately 10^{-5}–10^{-6} torr (1 torr = 1.333×10^2 Pa). The laser beam was focused at 45° to the target material by a CaF_2 lens until an energy density of 3–6 J cm^{-2} was obtained. The lens was mounted on a computer controlled X–Y table in order to scan the target laterally. The scanning combined with the rotation of the target created spiral scanning, causing each laser pulse to remove material from another area of the target. The ablated material was deposited on $SrTiO_3$ single crystal substrates which were glued to the heater with a conducting paint. XRD of a typical substrate is given in Fig. 3. The target–substrate distance was maintained at a distance of 2.5 cm and between them a d.c. bias operating at + 300 V was placed. The temperature of the heater was changed in a range 400–750 °C. The temperature was controlled by means of two thermocouples, one placed inside and the other on the

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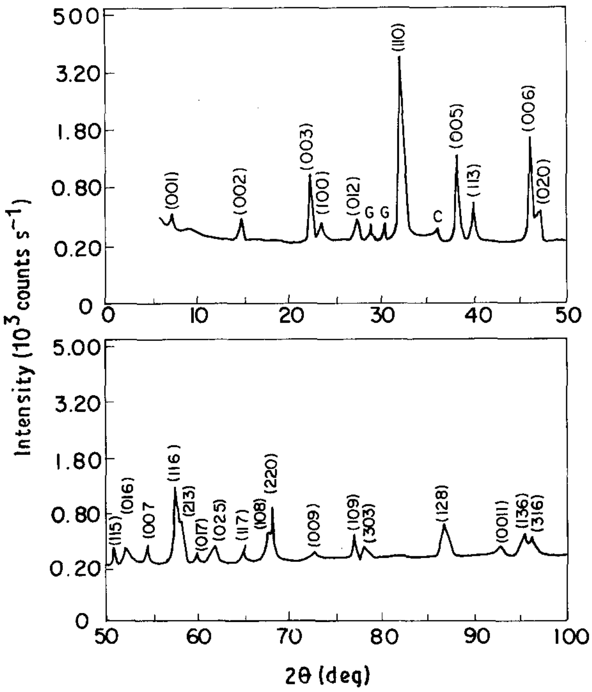

Figure 2 XRD spectrum of the target material. G, Y_2BaCuO_5; C, CuO.

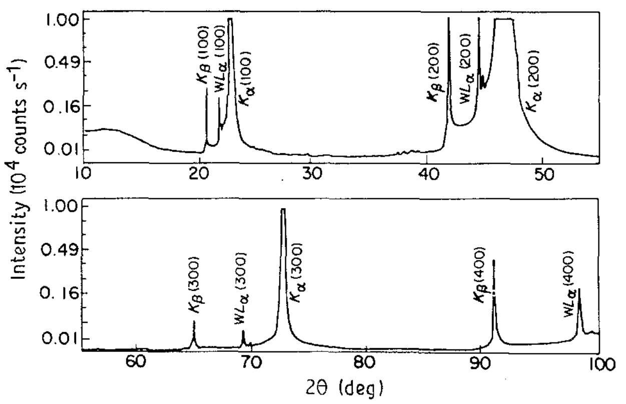

Figure 3 XRD spectrum of a typical $SrTiO_3$ (1 0 0) substrate.

heater's surface. It was possible to change the location of the heater in two perpendicular directions. During the process an oxygen pressure of 2×10^{-1} was maintained using high-purity oxygen (UHP 99.998%), which was introduced to the chamber through a needle valve. After 15 000–50 000 laser pulses at 1–7 Hz repetition rate, the deposition process was completed. The film thickness was 0.3–0.7 μm. Subsequently, the oxygen annealing process was carried out by filling the chamber with oxygen to atmospheric pressure and cooling the substrate to 420–500 °C for 30 min.

3. Results and discussion

Fig. 4a and b shows scanning electron micrographs, depicting the top and side views of a typical film, respectively. The film is continuous and crack free, spotted with small particles of 1–5 μm size (Fig. 4a). They were identified by energy dispersive spectroscopy (EDS) as target particles which were splashed

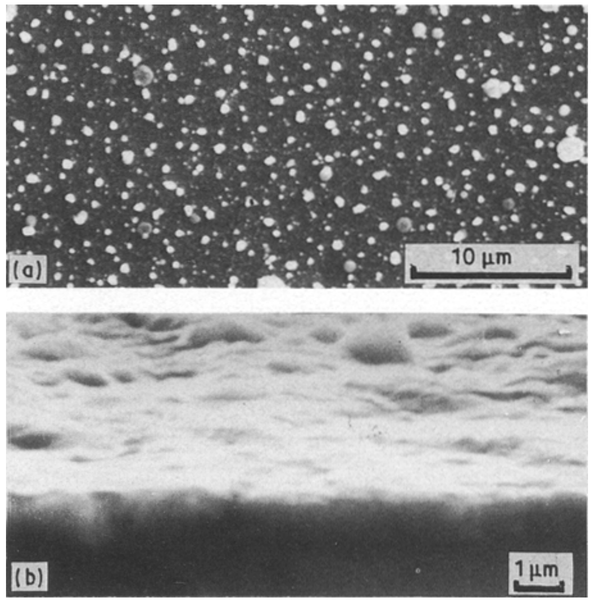

Figure 4 Scanning electron micrographs of a typical film. (a) Top view, (b) side view.

on the film during the laser ablation process. The side view on the film (Fig. 4b) shows its wavy shape.

Fig. 5 exhibits the composition depth profile of a typical film. The concentration of the various elements through the depth of the film is homogeneous.

The influence of the substrate temperature on phase composition and on the YBCO preferred orientation was studied by XRD. Fig. 6, for example, shows XRD patterns from films deposited at a repetition rate of 2 Hz at three different substrate temperatures. All the films consist of the YBCO phase; however, at a low substrate temperature of 470 °C (Fig. 6a), two other phases can also be observed; Y_2BaCuO_5 and CuO. These additional phases have been observed whenever

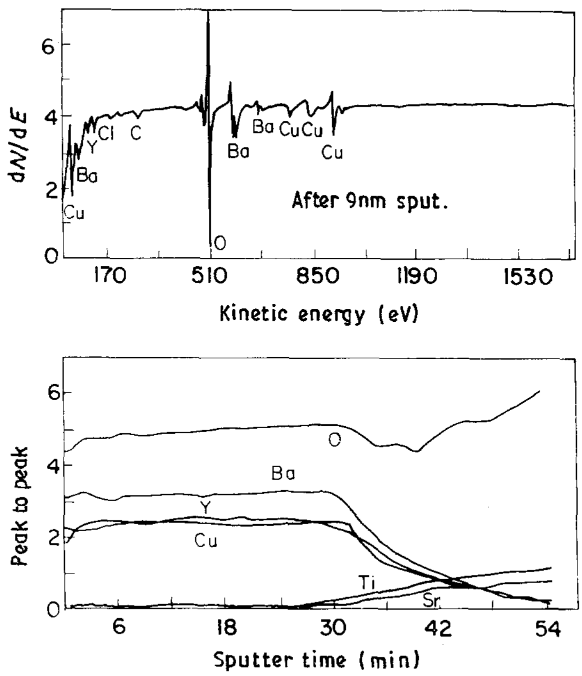

Figure 5 Auger electron spectroscopy compositional depth profile of a typical film.

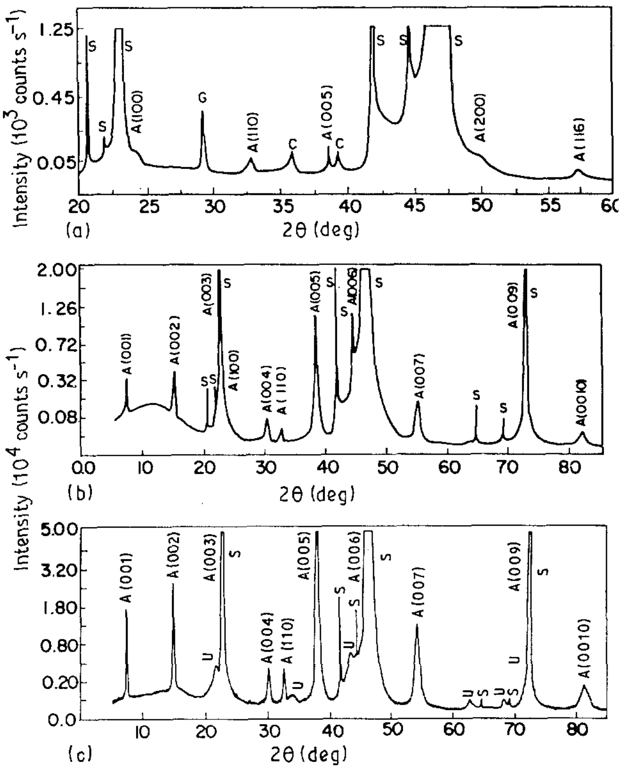

Figure 6 XRD spectrum of a film deposited on $SrTiO_3$ substrate at different temperatures. (a) 470 °C, (b) 600 °C, (c) 730 °C. The repetition rate was 2 Hz. S, $SrTiO_3$; C, CuO; G, Y_2BaCuO_5; A, $YBa_2Cu_3O_{7-x}$; U, $BaTiO_3$.

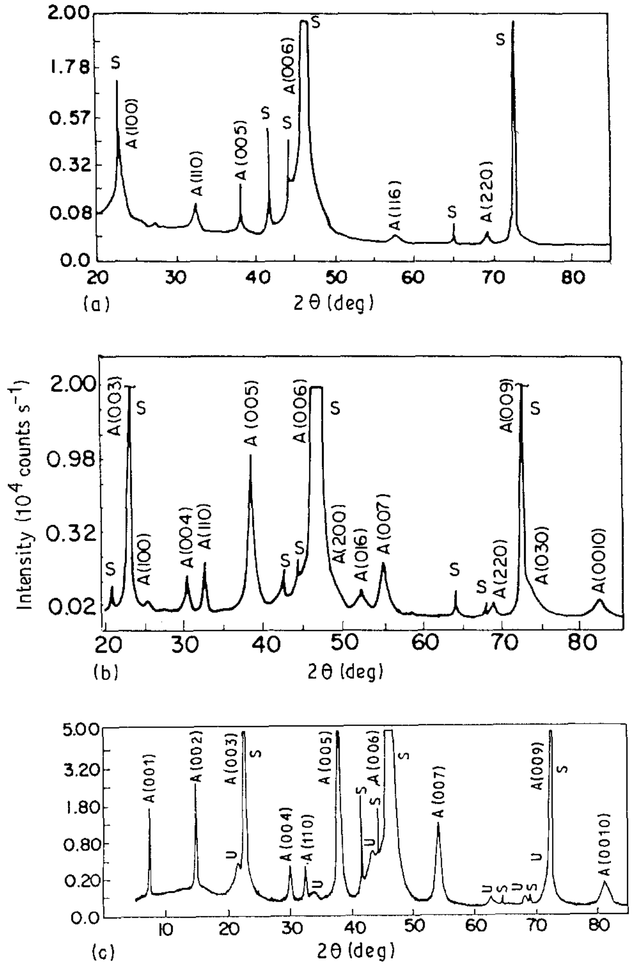

Figure 7 XRD spectrum of a film deposited on $SrTiO_3$ substrate with different repetition rates. (a) 7 Hz, (b) 2 Hz, (c) 1 Hz. The substrate temperature was 580–600 °C.

the substrate temperature was below 500 °C. At the higher substrate temperature of 600 °C (Fig. 6b) only the YBCO phase is observed. Most of the peaks are (0 0 *l*) peaks, indicating that the *c*-axis is normal to the films surface. There are also a few small (*h* 0 0) and (0 *k* 0) peaks which indicate that part of the film is oriented with the *a*- or *b*-axis normal to the surface, respectively. It is to be noted that the (1 1 0) peak which was the strongest one in the target material (see Fig. 2) is only a weak peak in the film. When the substrate temperature is 730 °C (Fig. 6c) the YBCO phase exhibits very sharp peaks as compared to the lower substrate temperatures. (For example compare (0 0 1), (0 0 2), (0 0 5) and (0 0 7) peaks of Fig. 6b and c.) In addition to the (0 0 *l*) peaks, no other peaks such as (*h* 0 0) or (*h k l*) could be observed, except (1 1 0). Although the YBCO film was well oriented, the relatively high substrate temperature caused the formation of $BaTiO_3$. This interface phase was probably created by substitution of Sr atoms of the substrate and Ba atoms of the film.

From the results described above one can conclude that there is an upper and lower substrate temperature limit within which only the YBCO phase exists. Within this range, the higher the substrate temperature the better the preferred orientation of the film relative to the substrate.

Fig. 7 shows the influence of the repetition rate on the film's composition at an almost constant temperature (580–600 °C). All the films consist of the YBCO phase only. For a repetition rate of 7 Hz (Fig. 7a) the film had all the high-intensity polycrystalline peaks. However, the (0 0 5) peak was higher than the (1 1 0) peak, which means that part of the film is preferentially oriented with respect to the substrate. For a lower repetition rate of 2 Hz (Fig. 7b) the film had all the (0 0 *l*) peaks, including (0 0 4), (0 0 7) and (0 0 1 0). These peaks do not exist in Fig. 7a. The peaks are sharper and the ratio between the (0 0 5) and (1 1 0) is larger. The alignment of this film was not perfect as could be seen from the (0 1 6) and (2 2 0) peaks. For a repetition rate of 1 Hz (Fig. 7c) the (0 1 6) and (2 2 0) peaks cannot be observed. In addition to the (1 1 0) peak there were only (0 0 *l*) peaks. These peaks were very sharp, compared to the peaks of Fig. 7b. The (0 0 4) peak is bigger than the (1 1 0) peak, contrary to that shown in Fig. 7b.

From the results presented above one can conclude that the lower the laser repetition rate the better the alignment and the preferred orientation of the film. One can assume that at low repetition rates the growth rate of the film is slow and therefore allows every deposited atom to be located at low-energy sites, i.e. good alignment with the substrate lattice. The influence of the substrate temperature on the films alignment with the substrate is similar, through the transfer of thermal energy to the deposited atoms in order to enable them to be located on low energy sites.

When the conditions are optimal the film is superconductive. The electrical resistance versus temperature of such a film is shown in Fig. 8. The electrical

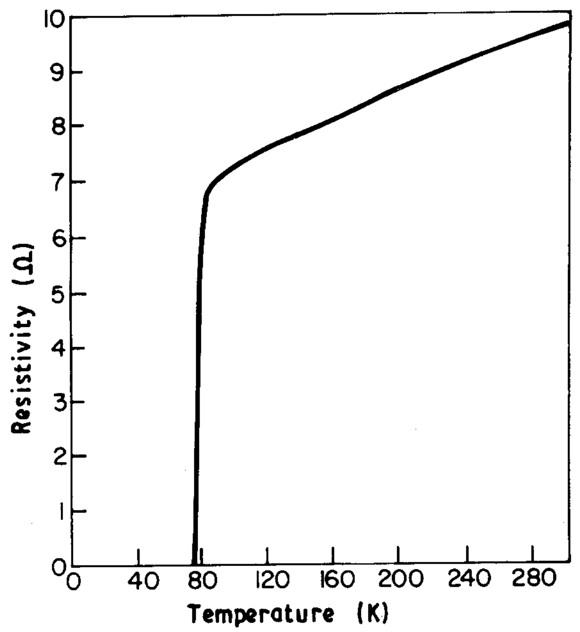

Figure 8 The variation of the electrical resistance with temperature for a film which was deposited on a $SrTiO_3$ substrate at the temperature of 700 °C, with repetition rate of 2 Hz.

resistance was measured by a four-point probe. The conditions for depositing this film were a substrate temperature of 700 °C and laser repetition rate of 2 Hz. The film thickness was 0.3 μm. The film is superconductive with a narrow transition range and a critical current density of 3.5×10^4 A cm^{-2} at 60 K.

4. Conclusions

In this investigation the optimal conditions for depositing superconducting thin films of $YBa_2Cu_3O_{7-k}$ on $SrTiO_3$ (1 0 0) substrate by means of pulse laser ablation technique was studied. The following conclusions can be drawn.

1. The composition of the film depends on the temperature of the substrate. When deposition is performed within the temperature range 500–700 °C the film consists only the superconductive YBCO phase. Lower substrate temperatures cause the formation of Y_2BaCuO_5 and CuO phases, while higher substrate temperatures cause the formation of $BaTiO_3$ phase.

2. The beam's repetition rate affects the alignment of the film. Low repetition rate as well as high substrate temperature created better conditions for highly oriented films.

3. The best condition for growing good superconductive films was found to be the substrate temperature of 700 °C and repetition rate of 1 Hz.

Acknowledgements

The authors thank Mrs S. Tamir, Mrs M. Rotel and Mr S. Altshulin for their help in the various stages of the study.

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Received 30 April
and accepted 6 June 1990.