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High rate deposition of thick epitaxial films by thermal plasma flash evaporation

Kazuo Terashima, Norio Yamaguchi, Tomoyuki Hattori, Yuzuru Takamura, and Toyonobu Yoshida

Department of Metallurgy and Materials Science, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT: Various thermal plasma deposition methods have been widely applied to high-rate and large-area preparation of high-quality films with special structures ranging from nano-crystalline to epitaxial. The thermal plasma flash evaporation (TPFE) method is one of the most promising ones for epitaxial film preparation. In this paper, our recent progress of the process characterizations of TPFE and its application to high-rate deposition of thick epitaxial $YBa_2Cu_3O_{7-X}$ films are reviewed. Special emphasis is given to the role of nanometer-scale clusters generated in a boundary layer between a plasma and a substrate in epitaxial film deposition.

I. INTRODUCTION

Recently, thermal plasmas have been applied to high-rate and large-area deposition of high-quality films with special structures ranging from nano-crystalline to epitaxial, owing to their high flux density of highly reactive particles, such as radicals. The thermal plasma flash evaporation (TPFE) method developed by our group, is one of the most promising methods for epitaxial film preparation(ref.1-19). Figure 1 shows a schematic model of this process, in which mixed fine powders of the constituents are continuously injected into a thermal plasma for complete coevaporation and codeposition onto a substrate. A radio-frequency (rf) plasma has been employed as the thermal plasma source for TPFE, because of its larger plasma volume and more uniform temperature field. So far, TPFE has been applied to prepare thin films of advanced functional materials such as superconductor and ferroelectric materials. In particular, it has successfully achieved the high-rate and large-area deposition of epitaxial films of multi-component systems such as $YBa_2Cu_3O_{7-X}$ (YBCO).

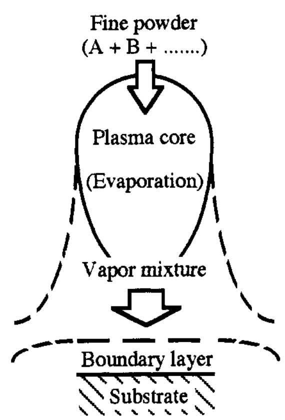


Fig.1 The schematic model of thermal plasma flash evaporation.

In this article, the recent progress of the TPFE technique and its application to the high-rate deposition of thick epitaxial films are reviewed mainly based on our data.

II. CHARACTERIZATIONS OF TPFE

TPFE is the modification of conventional flash evaporation, In which raw materials in their powdered form are dropped onto an evaporator in vacuum. In TPFE, the evaporator is replaced by a plasma flame and the powders are injected into the plasma under various reactive atmospheric or soft-vacuum conditions to be completely evaporated. Figure 2 represents a schematic setup of the apparatus of this novel processing technique. It may be said that the ability to cause vaporization is one of the most important features of this method. In order to achieve perfect evaporation of the powders, fine particles of less than 10 μm, must be fed continuously into the plasma with a precison similar to that achieved by the mass flow controller for gas feeding. This method has the following characteristics of typical rf thermal plasma processings (ref.20-22), in addition to the conventional flash evaporation method. (1) Composition-controlled high-temperature vapors can be generated easily. This makes it effective to synthesize multi-component films. (2) The raw materials are fine powders which do not include any other elements such as carbon in the metalorganic gas source for chemical vapor deposition (CVD). So, a reduction in the amount of contamination and by-products can be expected. (3) Any gas can be used as the plasma gas. (4) Owing to the high reactivity and high particle density of the rf plasma, a high deposition rate can be expected.

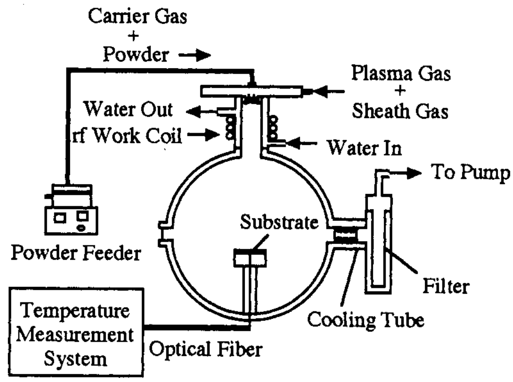


Fig.2 An experimental setup of thermal plasma flash evaporation.

We have developed this method to apply it to high critical temperature (T_c) superconductive film deposition, and obtained excellent YBCO films (T_c=92K, critical current density J_c=1MA/cm^2) as mentioned in the next section. Recently, the prominent features of TPFE have been revealed to be caused by cluster deposition under a high net flux of radicals such as atomic oxygen which actually reach a substrate through the boundary layer (ref.10,12,13). Nanometer-scale clusters as the deposition species are formed in the boundary layer under the high supersaturation of evaporated materials caused by quenching from 5000K to 1000K. The atomic oxygen flux was measured by a quartz crystal microbalance (QCM) as shown in Fig.3. The sensor made of a QCM covered with an Ag thin film was exposed to the plasma for a short period of time using a shutter. Ag is mainly oxidized by atomic oxygen, and the flux can be deduced from the small weight change (around 1 μg/cm^2) detected by the frequency change of the QCM. The comparison of the flux with other atomic oxygen sources is shown in Fig.4. The values are 10^3 times larger than those for the other sources using electron cyclotron resonance (ECR) plasma(ref.23), RF low-pressure plasma(ref.24), and microwave (MW) plasma(ref.25). These values correspond to the frozen atomic oxygen fraction around 7%. These results show the high particle density of highly reactive radicals in this process. On the other hand, as shown in Fig.5, a micro-trench method

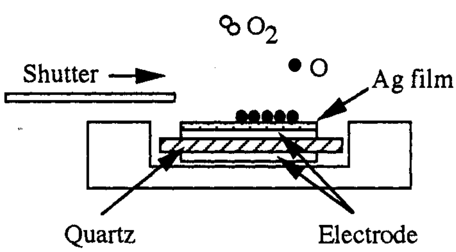


Fig.3 A schematic of the atomic oxygen measurements, a using quartz crystal microbalance.

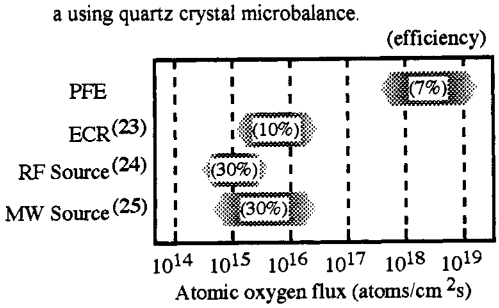


Fig.4 A comparison of atomic oxygen sources.

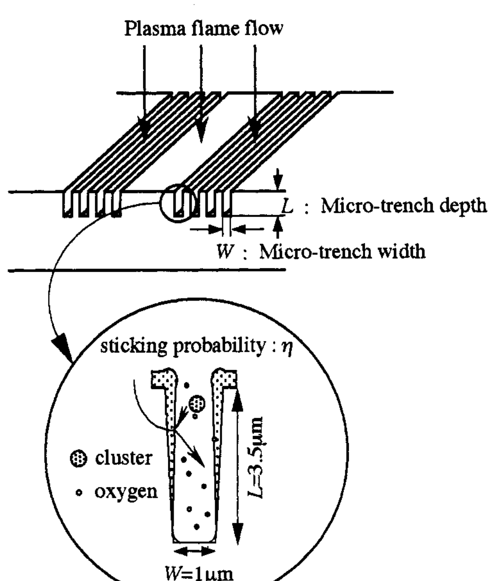
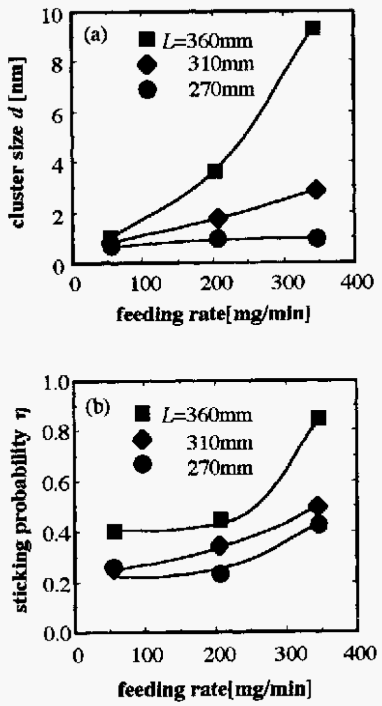


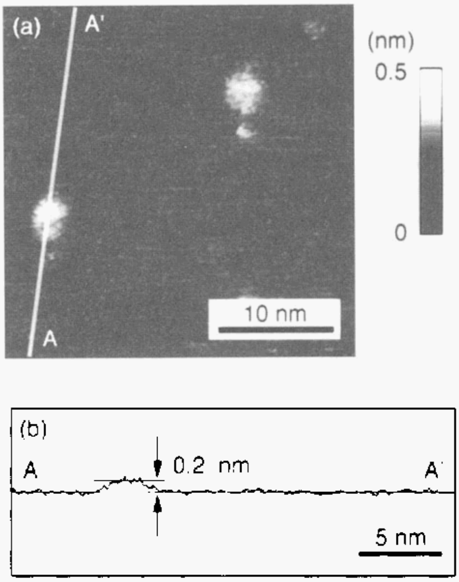
Fig.5 A schematic diagram of the microtrench method.

has been developed in order to obtain the information of the deposition species in this process. In this method, the size (d) and sticking probability (η) of the deposited species can be obtained from the profile of films deposited inside a microtrench fabricated on a Si wafer. By this method, the size of the YBCO deposited species was estimated to be about 0.3 to 10 nm by controlling the quenching rate and concentration of the vapor phase species. Figs. 6 (a) and (b) show the typical results of d and η as a function of feeding rate for 3 torch-substrate distances (L).

Moreover, the STM measurements reconfirm directly that the deposition species in this process are the clusters(ref.12,14). The clusters have interesting characteristics as deposition species as follow ; (A) They have a higher sticking probability than atoms, especially at high temperatures. (B) They are activated and unstable clusters, which are expected to be rearranged easily into the stable or quasi-stable structure on a substrate. The clusters undoubtedly involve a considerable amount of internal energy necessary for crystallization at the substrate and exhibit considerably different characteristics from those of the clusters generated in vacuum by an adiabatic expansion process such as those in the ionized cluster beam (ICB) method(ref.26). We call this cluster a "hot cluster"(ref.12,14). It is revealed that this deposition process from hot clusters with a large-sticking-probability onto a substrate even at high temperatures is highly effective for the high-rate deposition of high-quality films. A novel epitaxial growth mechanism from hot clusters, "Hot Cluster Epitaxy" is also proposed as follows; (1) Species with "hot" clusters are introduced at a high concentration onto a substrate. (2)The small "hot" clusters can be easily rearranged. (3) The cluster may act as the nuclei or steps needed for crystal growth, which results in a high deposition rate even at high substrate temperatures. (4) A high substrate temperature activates the surface migration of clusters and atoms, which results in good quality films, such as epitaxial films, with an extremely high deposition rate. From the STM measurements, we clarified the rearranged cluster, as shown in Figs.7(a) and (b), and the lateral growth mechanism from clusters depending on the cluster size as shown in Fig.8. As expected, almost all the clusters are two dimensional, nearly disk-shaped and have a height of approximately one monolayer, which means that the hot clusters easily deform into two-dimensional (2D) structures even on room-temperature substrates(ref.14). On



Figs.6 (a) Size(d) and (b) sticking probability (η) of YBCO deposited species as function of the feeding rate for some torch-substrate distance (L).



Figs.7 (a) Typical STM image and (b)the cross-section along A-A' line of clusters of as-deposited species on a room-temperature substrate.

the other hand, a theoretical analysis based on the comparison of the 2D critical radius (r^*_{2D}) with 2D cluster radius (r_{2D}) revealed tha change of tha lateral growth mode from spiral growth to 2D nucleas growth(ref.12). Small clusters ($r_{2D} < r^*_{2D}$) are to be re-evaporated on the crystal surface, and trapped at the steps, similarly to the growth from atoms, resulting in spiral growth. While, larger clusters ($r_{2D} > r^*_{2D}$) are can be stable nuclei resulting in 2D nucleus growth. This mechanism may enable the deposition of high-quality epitaxial "thick" films, because of the high deposition rate.

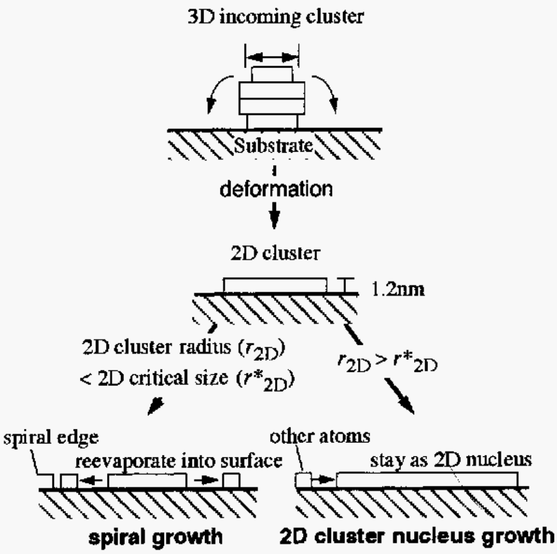


Fig.8 The concept of lateral growth mechanism from clusters.

III . APPLICATION TO HIGH-RATE DEPOSITION OF EPITAXIAL THICK FILMS

We have developed this process especially, the hot cluster epitaxy mode, to apply it to high T_c superconductive film depositions, and we obtained as-grown epitaxial $YBa_2Cu_3O_{7-X}$ films with excellent properties (T_c=93K, J_c= 1 MA /cm^2 at 77K under zero magnetic field) at a high deposition rate, above 0.1 μm/min on $SrTiO_3$ (STO) substrates over an area of 7 x 7 cm^2 as expected. Figure 9 shows the typical STM image of the film deposited on a STO substrate at a substrate temperature of T_s=1073 K. The growth rate was 1 μm/min, which is 10-1000 times faster than that of other conventional epitaxial techniques, such as MBE and sputtering. In spite of such a high deposition rate, the film surface was atomically flat with the terrace structures of step-height 1.2 nm, corresponding to a c-lattice constant of YBCO. Figure 10 shows a (205) X-ray pole figure, exhibiting excellent epitaxy. Moreover, the full width at half maximum (FWHM) of the rocking curve of the X-ray diffraction (XRD) (005) peak was extremely narrow, about 0.14°. The value is one of the smallest ones reported for films so far(ref.27,28). These facts reconfirm the advantages of this processing method, namely high-rate deposition with the high-quality epitaxial structure, overcoming other conventional methods. Taking the application of superconducting films to power electronics such as superconductive tape and wire into account, the fabrication of epitaxial thick films is desired. At this stage, a 6-μm-thick epitaxial $YBa_2Cu_3O_{7-X}$ film with a FWHM of 0.25° of the X-

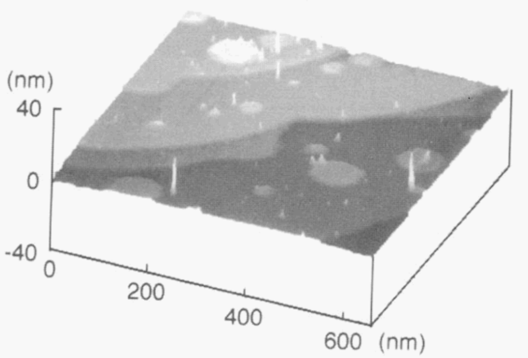


Fig.9 STM image of a 1-μm-thick epitaxial YBCO film with the deposition rate of 1 μm / min.

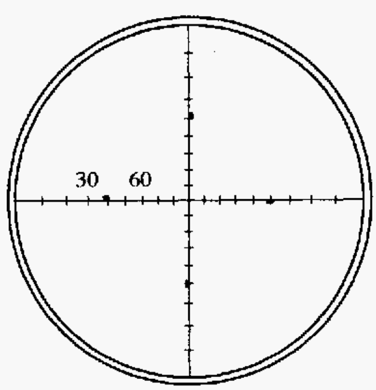


Fig.10 (205)X-ray pole figure.

ray rocking curve has been successfully deposited at the high rate of 0.3 μm/min. These films also have a T_c exceeding 90K and J_c values around $10^5 A/cm^2$ at 77K. These values are comparable to those obtained by the other most promising epitaxial method for obtaining thick films, liquid phase epitaxy (LPE) (ref.29), in which a long duration of after-annealing of about 24 hours is required.

In today's frontier materials processing technology, epitaxial film formation techniques have been indispensable and many processes, such as MBE, CVD, and laser deposition, have been successfully developed. However, the established processes have been limited to epitaxial thin ($<1\ \mu m$) film deposition and the microelectronics field such as for memory storage devices, due to their low-deposition rate of typically 0.01 μm/min. The establishment of epitaxial thick film processing is expected to open up the new aspects of various high-technological fields, such as power-electronics, optoelectronics, and micro-mechatronics. These results demonstrate not only the success of high-rate epitaxial YBCO film deposition but also the potential of epitaxial thick film technology.

IV. CONCLUSIONS

In this article, we briefly review the thermal plasma flash evaporation (TPFE) method for epitaxial film formation. Special emphasis is given to the application of the high rate deposition of YBCO epitaxial thick films, relating to the role of nanometer-scale clusters generated in a boundary layer between a plasma and a substrate during high-rate epitaxy. A novel epitaxial growth mechanism from the "hot" clusters namely "hot cluster epitaxy (HCE)" is introduced.

Without a doubt, TPFE will open up new fields of film deposition such as "Epitaxial Thick Film Technology" in the near future.

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