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APPLICATION OF RADIO-FREQUENCY (RF) THERMAL PLASMA TO FILM FORMATION

Kazuo Terashima and Toyonobu Yoshida

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

ABSTRACT

Several applications of radio-frequency (RF) thermal plasma to film formation are reviewed. Three types of injection plasma processing (IPP) technique are first introduced for the deposition of materials. Those are thermal plasma chemical vapor deposition (CVD), plasma flash evaporation, and plasma spraying. Radio-frequency (RF) plasma and hybrid (combination of RF and direct current(DC))plasma are next introduced as promising thermal plasma sources in the IPP technique. Experimental data for three kinds of processing are demonstrated mainly based on our recent researches of depositions of functional materials, such as high temperature semiconductor SiC and diamond, ionic conductor ZrO_2–Y_2O_3, and high critical temperature superconductor $YBa_2Cu_3O_7$-x.

Special emphasis is given to thermal plasma flash evaporation, in which nanometer-scaled clusters generated in plasma flame play important roles as nanometer-scaled clusters as deposition species.

A novel epitaxial growth mechanism from the "hot" clusters namely "hot cluster epitaxy (HCE)" is proposed.

INTRODUCTION

Recently, radio-frequency (RF) thermal plasmas have been applied to plasma processing, especially injection plasma processing (IPP) for high-rate and large-area depositions[1]. Compared to conventional direct-current (DC) thermal plasma, RF the-rmal plasma has many advantages as plasma source for deposition, such as larger plasma volume and more uniform temperature field. High performance films of advanced functional materials such as high temperature semiconductor diamond and SiC[2-6], high critical temperature superconductor $YBa_2Cu_3O_{7-x}$[7-17], and ionic conductor ZrO_2–Y_2O_3 for solid oxide fuel cells (SOFC)[18,19] have been successfully synthesized by the RF-IPP.

In this paper, the recent progress of the RF-IPP is briefly reviewed mainly based on our researches.

RF INJECTION PLASMA PROCESSING (RF-IPP) FOR DEPOSITION

Roughly speaking, the present thermal plasma processing can be classified into two categories, which originated from batchtype arc heating processing and combustion processing. Injection plasma processing (IPP) may be classified into a new branch of the latter case.

IPP for film deposition can be divided into three main categories (Fig. 1). The thermal plasma CVD (TPCVD) is characterized by the injection of gaseous or liquid reactants into the plasma. The second is plasma flash evaporation, in which fine powder mixtures of constituents are continuously injected into the thermal plasma and are co-evaporated and co-deposited onto a substrate. The last one shows plasma spraying. In this case, coarse powders are injected. The injected powder size must be large enough not to be vaporized, and small endough to be completely melted. Each droplet is flattened on impact at the substrate and solidified, and the coating consists of many layers of flattened particles. This method has been used for over two decades in applying metals and ceramics coatings.

The most inportant key to success for IPP in various coating applications depends to a large extent upon the development of thermal plasma torches which make it possible to generate relatively large size plasma with more uniform profile of velocity, temperature, chemical species, and to sustain a stable plasma. In these respects, an RF plasma torch and hybrid (combination of RF and direct current (DC)) plasma torch are strongly recommended, compared to conventional DC plasma torch. Actually, the effectiveness of these two kinds of plasma torches for deposition has been widely accepted by industries which have developed industrial scale torches with the power level higher than few hundreds kW.

In our group, applications of the RF-IPP to functional film formation have been intensively performed in the last decade.

A prominent feature of TPCVD is considered to be an extremely high flux of radicals, which results in high-rate deposition. The high-rate deposition at a rate above 200nm/s of diamond and SiC[2-6] have been successfully performed. Moreover, in order to apply this process for large-area deposition, we have been developing a cyclic-TPCVD(C-TPCVD) system consisting mainly of a hyb-

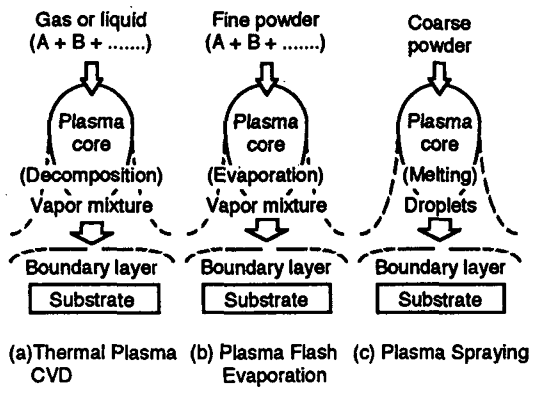

Fig. 1 Three main categories of IPP for deposition

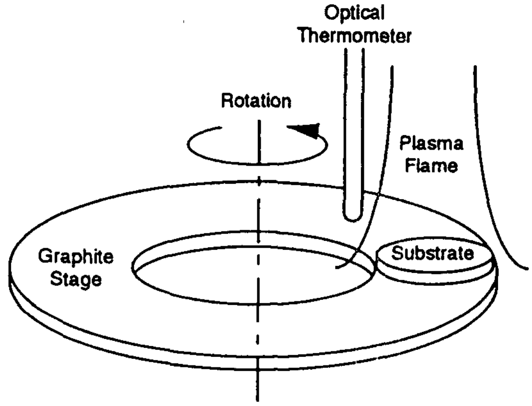

Fig. 2 Schematic diagram of cyclic thermal plasma CVD(C-TPCVD).

rid torch and a deposition chamber in which a 300 mm outside-diameter rotating dough-nut-type gra-phite stage is set up (Fig.3)[5-6].

The plasma flash evaporation method developed by our group has following interesting characteristics of typical RF thermal plasma processing, in addition with the conventional flash evaporation method;(1) Generation of composition-controlled high-temperature vapors. (2) Minimization of by-products. (3) Flexibility in the choice of the gas to be used as a plasma gas. (4) Owing to the high reactivity and high ability of throughput, high-rate deposition can be expected. We have developed this method to apply to high critical temperature (Tc) superconductor film deposition, and obtained excellent (Tc= 92K(Fig. 3), critical current density Jc=1MA /cm^2 at 77K) $YBa_2Cu_3O_{7-x}$[7-17] with a high deopsition rate, above 1μm/min. The prominent mechanism of this process is that of cluster deposition under a high net flux of atomic oxygen (Fig. 4). In the next chapter, the mechanism of deposition from clusters will be described.

As mentioned previously, plasma spraying has been used for over two decade for metals and ceramics coatings. In conventional atmospheric DC plasma spraying(APS), how-ever, the structure of the coating is somewhat porous and the bonding strength is not so satisfactory.

To overcome these shortcomings, a relatively new technology, namely low pressure plasma spraying (LPPS) has been developed recently. Unfortunately, LPPS also has shortcomings, that is, lower momentum and heat transfer to the particles than for APS, and there still remain many problems concerning spraying of ceramics such as ZrO_2. From the points of view mentioned above, RF plasma spraying (RFPS) and hybrid plasma spraying (HYPS) have been developed[20,21]. The large plasma volume and capability for axial injection were expected to reduce the trajectory variation and to reduce the porosity. We have successfully deposited ZrO_2-Y_2O_3 thick film for solid oxide fuel cells (SOFC) by HYPS[18,19].

HOT CLUSTER EPLTAXY(HCE)

Very recently, the prominent feature of plasma flash evaporation method was revealed to be deposition from clusters[13-16].

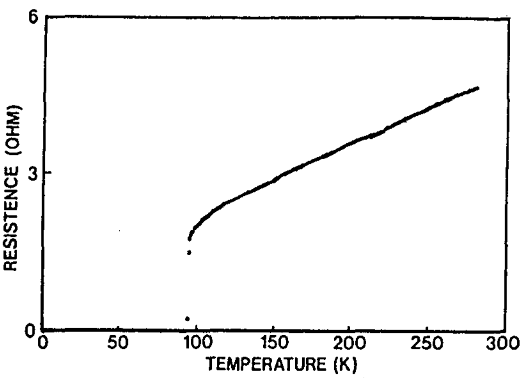

Fig. 3 Temperature dependence of electric resistance of YBCO films prepared by plasma flash evaporation.

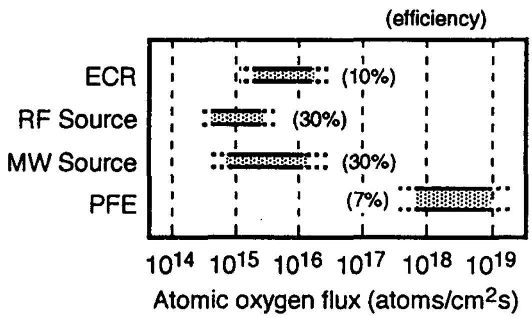

Fig. 4 Comparison of various plasma sources of atomic oxygen.

Nanometer-scale clusters are formed in the boundary layer under the high supersaturation of evaporated materials caused by quenching from 5000K to 1000K. By micro-trench method, we succeeded in measuring the cluster sizes. In this method, cluster size can be obtained from the film profile inside a micro-trench(Fig.5)[13,14].
The cluster size of YBCO was estimated to be about 0.3 to 10 nm by controlling the quenching rate and concentration of vapor phase species. The clusters have interesting characteristics as deposition species as follows:

1) They have a high sticking probability than atoms, especially at high temperatures.

2) They are activated and unstable "hot" cluster, which are expected to be rearranged easily into the desired structure on a substrate.

3) They play the roles of unclei for crystal growth of films.

Actually, from the STM measurements, we clarified the lateral growth mechanism from clusters depending on the cluster size(Fig. 6).

Moreover, we proposed a new epitaxy, namely "Hot Cluster Epitaxy" as follows[15,16]:

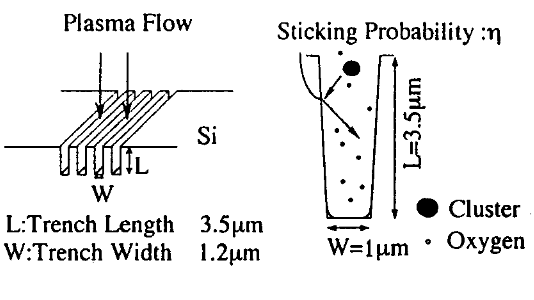

Fig. 5 Principle of the micro-trench method for cluster size measurement.

1) Species with "hot" clusters are introduced at a high concentration onto a substrate.

2) The small "hot" clusters can be easilly 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 temperature.

4) High substrate temperature activates surface migration of clusters and atoms, which results in good quality of films, such as epitaxial film, with an extremely high deposition rate.

At this stage, a 1 μm-thick, smooth monolayer epitaxial film of YBCO with a full width at half-maximum(FWHM) of less than 0.14° of X-ray rocking curve was successfully deposited at the high rate of 16nm/s. This mechanism may enable the deposition of multicomponent high-quality epitaxial "thick" films, because of the high deposition rate. These features can't be performed by conventional epitaxial deposition

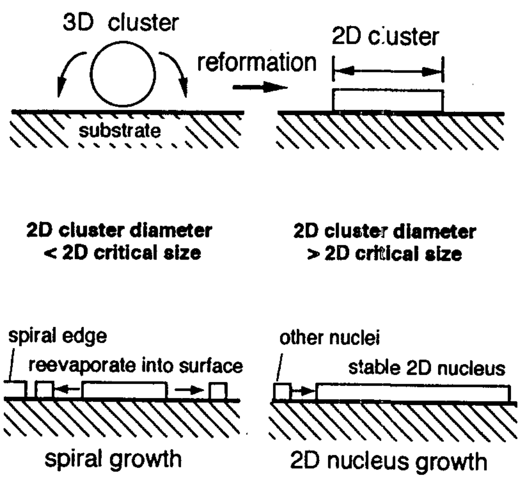

Fig. 6 Lateral growth mechanism from clusters.

method such as molecular beam epitaxy (MBE).

SUMMARY

In this article, we briefly review the promising RF injection plasma processing(IPP) technique for film formation. Three types of RF-IPP, that is, RF thermal plasma chemical vapor deposition (CVD), RF thermal plasma flash evaporation, and RF thermal plasma spraying are characterized. Special emphasis is given to RF thermal plasma flash evaporation, in which nanometer-scaled clusters generated in plasma flame play important roles as nanometer-scaled clusters as deposition species. A novel epitaxial growth mechanism from the "hot" clusters namely"hot cluster epitaxy (HCE)" is proposed.

Without a doubt, these three RF IPP techniques will open new fields of deposition such as "Epitaxy Thick Film Technology" in the near future.

REFERENCES

1. T. Yoshida, Pure & Appl. Chem. **6**, (1994) 1223
2. S. Matumoto, M. Hino and T. Kobayashi, Appl. Phys. Lett. **51**, (1987) 737
3. H. Murakami, T. Yoshida and K. Akashi, Advanced Ceram. Mater. **3**, (1988) 423
4. H. Murakami, K. Eguchi, and T. Yoshida, J. Japan Inst. Metals, **56**, (1992) 452
5. K. Eguchi, S. Yata, and T. Yoshida, Appl. Phys. Lett. **64**, (1994) 58
6. H. Yin, K. Eguchi, and T. Yoshida, J. Appl. Phys. **78** (1995) 3540
7. K. Terashima, K. Eguchi, T. Yoshida, and K. Akashi, Appl. Phys. Lett., **52**(1998) 1274
8. K. Terashima, H. Komaki, and T. Yoshida, IEEE Trans. Plasma Sci., **18** (1990) 980
9. K. Terashima, T. Akagi, H. Komaki, and T. Yoshida, J. Appl. Phys., **71** (1992) 3427
10. S. Yuya, K. Kikuchi, Y. Shiohara, K. Terashima, and T. Yoshida, J. Mater. Research, **8**, (1992) 2673
11. Y. Takamura, Y. Hirokawa, H. Komaki, K. Terashima, and T. Yoshida, Physica C**190** (1991) 122
12. Y. Hirokawa, Y. Takamura, H. Komaki, K. Terashima, and T. Yoshida, J. Mater. Synthe. Process., **1** (1993)
13. Y. Takamura, K. Hayasaki, K. Terashima, and T. Yoshida, Plasma Chem. Plasma Process., **16** (1996) 141s
14. Y. Takamura, K. Hayasaki, K. Terashima, and T. Yoshida, to be published in J. Vac. Sci. Technol. A
15. Y. Takamura, N. Yamaguchi, K. Hayasaki, K. Terashima, and T. Yoshida, and T. Yoshida, submitting to Appl. Phys. Lett.
16. K. Hayasaki, Y. Takamura, N. Yamaguchi, K. Terashima, and T. Yoshida, submitting to J. Appl. Phys.
17. K. Terashima, M. Kondoh, Y. Takamura, H. Komaki, and T. Yoshida, Appl. Phys. Lett., **59** (1991) 644
18. H. Hamatani, H. Kumaoka, T. Yahata, and T. Yoshida, J. Japan Inst. Metals, **55** (1991) 1240
19. T. Yoshida, T. Okada, H. Hamatani, and H. Kumaoka, Plasma Source Aci.

Technol., 1 (1992) 195
20. J. Jurewicz, R. Kaczmarek, and M. I. Boulos, Proc. 9th INt. Symp. Plasma Chem. (ISPC9),ed. C. J. Timmerans, Eindhoven Netherland, (1985) 1131
21. S. Takeuchi, T. Okada, T. Yoshida, and K. Akahi, J. Japan Inst. Metals, 52 (1988) 711