CNIC-00511
ASIPP-0027

中国核科技报告

微波 ECR 等离子体物理汽相沉积研究和应用

INVESTIGATION AND APPLICATION OF MICROWAVE ELECTRON CYCLOTRON RESONANCE PLASMA PHYSICAL VAPOUR DEPOSITION

原 子 能 出 版 社

中国核情报中心
China Nuclear Information Centre

CNIC-00511
ASIPP-0027

微波ECR等离子体物理汽相沉积研究和应用

任兆杏　盛艳亚　史义才　闻海虎　曹效文

（中国科学院等离子体物理研究所）

摘　要

研究了用微波电子回旋共振(ECR)技术蒸发镀Ti膜、Cu膜。沉积速率达50.0 nm/min左右，基片温度50～150℃。获得了附着力强的非晶态膜层。进行了ECR溅射镀膜，采用较高的等离子体密度、电离度及负的基片电位，制作了YBaCuO超导薄膜。该膜层致密、呈非晶态、膜厚1.0 μm，沉积速率达10.0 nm/min。结果表明，ECR等离子体沉淀技术是能够在低压下产生高密度、高电离度的等离子体，这种等离子体是薄膜沉积工艺和表面处理技术中最合适的等离子体源。

INVESTIGATION AND APPLICATION OF MICROWAVE ELECTRON CYCLOTRON RESONANCE PLASMA PHYSICAL VAPOUR DEPOSITION

Ren Zhaoxing Sheng Yanya Shi Yicai
Wen Haihu Cao Xiaowen
(INSTITUTE OF PLASMA PHYSICS, ACADEMIA SINICA)

ABSTRACT

The evaporating deposition of Ti film and Cu film by using microwave electron cyclotron resonance (ECR) technique was investigated. Its deposition rate was about 50 nm/min and the temperature of the substracte was 50～150℃. The thin amorphours films with strong adherent force were obtained. The sputtering deposition with ECR plasma was studied employing higher plasma density and ionicity and negative substrate potential to make YBaCuO superconducting film. Its film was compact and amorphours with a thichness of 1.0 μm and the deposition rate was about 10 nm min. The results show that this technique can initiate a high density and high ionicity plasma at lower gas pressure(10^{-2}～10^{-3}Pa). This plasma is the most suitable plasma source in thin film deposition process and surface treatment technique.

INTRODUCTION

Recently for twenty years, some kinds of discharge excited at lower gas pressure already have widely and successfully been applyed to the surface technology, such as thin film deposition and surface etching. In this technology the plasma played an important role and the plasma parameters served considerable function of thin film quality. That is , the plasma characteristic parameters to be requested in the deposition and the etching are enhanced with the advance of the qualitative requirements.

The plasma adopted in the surface technique is commonly excited by direct current (DC) or radial frequency (RF) discharge in a chamber with gas pressure region 1～100Pa. DC glow discharge was first employed to thin film technique. However this plasma is a discharge not only with electrodes, but also with lower density, lower ionicity and higher operating pressure. That is, the applicable area is much more limited. Since the late 1940s, many investigators had performed a number of study for RF discharge, which was applyed to semiconductor film deposition technique until the middle of 1960s. Since then RF plasma deposition technique was developed conseqeuntly and got wide application. RF plasma appears the features of electrodeless discharge and eliminates the pollution of impurities from electrode. But, it also is a lower density and ionicity plasma and operates at higher gas pressure, therefore the thin film quality deposited with RF plasma is considerablely not improved yet.

Table 1. comparison of DC, RF, and ECR discharge

Plasma parameter	DC discharge	RF discharge	ECR discharge
Discharge frequency (MHz)	DC	13.56	2450
Electron temperature (eV)	several	several	several-tens
Gas pressure (Pa)	1～100	1～10	0.001～0.1
Electron density ($10^{10}cm^{-3}$)	0.1～1	～1	10～100
Gas ionicity (%)	<0.1	1	20～50

Recentey for ten years, by reason of the microwave ECR plasma has been introduced in coating technique, great enhancing thin film quality can be realized, because the ECR plasma has more excellent plasma characters than the DC plasma or the RF plasma.

Table 1. shows the ECR plasma not only has higher density and ionicity, but also can operate at lower gas pressure, so that it is a ideal plasma source applying to the surface technique. The ECR plasma deposition may adopt the methode of chemical vapour deposition or physical vapour deposition in order to meet different requirements. The technique of ECR plasma chemical vapour deposition (ECRPCVD) was described by Ref. [1]. This paper attachs importance to introduce the technique of ECR plasma physical vapour diposition (ECRPPVD). According to the different methods of vapouring film material, we introduce the evaporation with microwave ECR plasma in the second section and the sputtering deposition with it in the third section. Fourth section gives how to deposit YBaCuO superconducting thin film with the sputtering method. The last section gives the summarize.

1 EVAPORATING DEPOSITION WITH ECR PLASMA

The principle of common evaporation is that, the film material in vacumm chamber is first heated and vapourized, then its vapourized atoms are directly deposited on the spectimen. The major fault of this technology is lower adherent force between the film and the substrate and bad bulk film density. If a weak ionization plasma is applied to evaporating deposition, the thin film quality will be improved, but can not satisfy more advance requirements for developing thin film technique.

The HER mirror machine[2] is employed as a evaporating depositing apparatus with microwave ECR plasma as depicted in Fig. 1). A magnetron launcher is applyed to produce 0~2kW power microwave with 2450MHz frequency, which is transmitted through the rectangular waveguides with dimension 12cm × 6cm and is injected into the cavity through the window of PTPF (polytetrafluoroethylene). When the magnetic field strength is selected suitablely, the resonance is taked place between the wave and the electrons, which is accelerated. The energatic electrons come into collision and ionization with the atoms of Ar gas (0. 01Pa) puffing in the cavity, the dense plasma will be formed. The film material for deposition is heated and vapoured by vapourizing vessel set in the lowest of the cavity or by derect current through a wire (for example, Ti-Ta wire), Its molecules or atoms go into ECR discharge region, then the plasma involving film material component is formed. The film material ions are confined by magnetic field and go to on the substrate under the function of a negative potential from specimen table. Then the thin film is deposited.

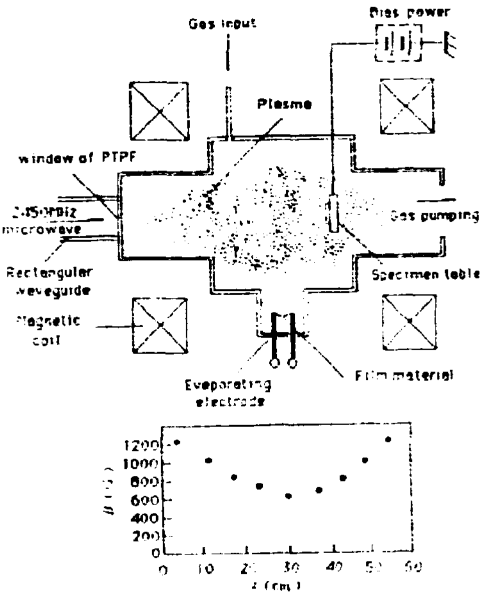

Fig. 1 Schematic diagram and magnetic field distribution of evaporating deposition with microwave ECR plasma

Utilizing this machine, the dense Ti film and Cu film wih strong adherent force are deposited. Its deposition rate was about 50 nm/min and the specimen temperature was in the regiop from 50℃ to 150℃. Those parameters show that the main feature of this technology is that the thin film with strong adherent force can fastly be deposited in low temperature. The coating thin films are analysed by XRD pattern. The film on the quartz substrate is a amorphours constructure.

2 SPUTTERING DEPOSITION WITH ECR PLASMA

Because evaporation has some limitation, namely it is difficut that the thin films with high melting point and low vapourizing pressure and some compound films are made by this method. An advenced sputtering deposition technique have been developing after some scientists' studies for long time. At present it have been applying to various film deposition. However the reactive energy of classical sputtering deposition technology at forming thin film does not be selected and controlled adqautely, it is more difficult for deposition of metal film and metal-compounned film especially. The classical sputtering deposition technology have another both hard problem still:

(1) Lower deposition rate, that is low efficiency;

(2) The substrates must be heated for making higher quality.

We applied microwave ECR plasma technique to sputtering deposition technology and developed out the technology of microwave ECR plasma sputtering deposition. The schametic drawing of the experimental apparatus is shown in Fig. 2. The microwave with frequency 2450 MHz is transmitted through the rectangular waveguides and is injected into the plasma chamber used as the microwave resonance cavity through a quartz window. The magnetic coils around the chamber provide the typical divergent magnetic configuration for ECR. The resonance layer wigh 0.875 T of magnetic field causes the electrons in plasma to absorb microwave energy at $10^{-3} \sim 10^{-1}$Pa of low pressure. The operating gas Ar is injected into the plasma chamber, the reactive gases (for example, O_2, N_2, CH_4, et al.)is fed to the specimen chamber. They can be ionized to form high density and high ionicity plasma. A sputtering target is set at the exit of plasma stream and is biased a high negative voltage (0~1kV), which can cause the ion in plasma to compact the target, so that the plasma sputtering occured. The film material atoms sputtered from target go into the plasma and are ionizated in collision with cyclotron electron to become the film material ions, which can be confined by the magnetic field and accelerated by a negative potential on the substrate, then arive on it.

Because of the higher plasma density and ionicity and the negative substrate potential, the compacting and reactive effects of the ion on the substrate surface are enhanced at the deposition, so that this technology may deposit high quality thin film at lower temperature with the higher sputtering rate than other methods. We employed this apparatus to deposit some films, for example, Cu film, metal oxide film, and especially to deposit successfully YBaCuO superconducting film[3].

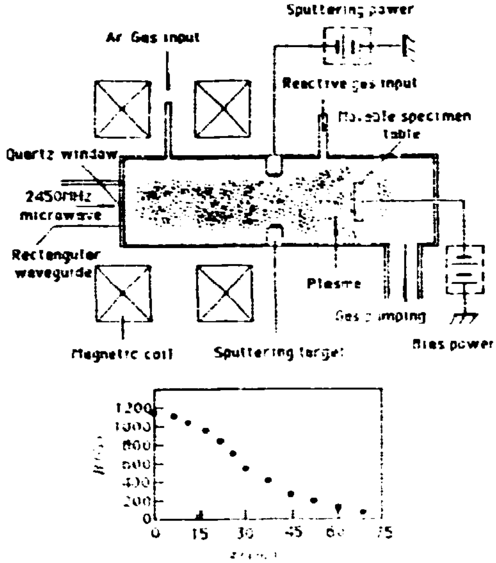

Fig. 2 Schematic diagram and magnetic field distribution of sputtering deposition with microwave ECR plasma

3 DEPOSITION OF YBaCuO SUPERCONDUCTING FILM

Study and preparation of high T_c oxide film are very important for both science and technology. Up to now, though a number of techniques can be used to fabricate high T_c superconducting film (for example: e-beam and thermal co-evaporation[4-6], magnetron sputtering[7,8], molecular beam exitaxy[9] and pulsed laser ablation[10] etc.), people have ever been seeking a much more perfect manufacturing method for increasing deposition rate, improving quality of film, direct deposition at oxygen gas atmosphere, realizing large area coating film etc.. Microwave ECR plasma coating seem could completely satisfy above requirements.

In the experiments of coating superconducting film, many operating parameters could be adjusted, for example, magnetic field configuration, total pressure p, ratio of p_{Ar} to p_{O_2}, microwave power P_{in}, location of resonance layer (magnetic field coil's current I_M), distance d between target and substrates, target voltage V_t, target current I_t, substrate potential V_s, component of Y-Ba-Cu-O superconducting material target, substrate temperature and etc. We have not only checked the superficial qualities (for example; adhension, compactness, uniformity and etc.), superconductivity and so on, but also investigated the relations between the film quality and the operation parameters.

3.1 Relationship between V_t and I_t

Figs. 3~6 show the relations of V_t - I_t for four different parameters. The sputtering rate has related to both V_t and I_t. V_t is limited by insulating ability between target and vacuum chamber, but I_t depends on selecting of P_m, I_M, p_{Ar} and p_{O_2}. For getting highest sputtering rate, adequate P_m, I_M, p_{Ar} and p_{O_2} are operated.

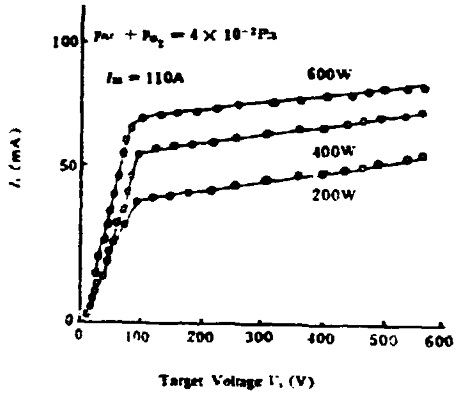

Fig. 3 Relationship between target current and voltage for several microwave power

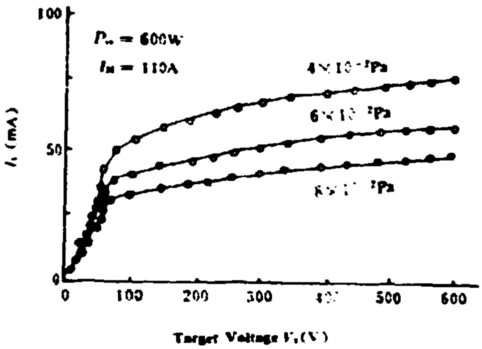

Fig. 4 Relationship between target current and voltage for several operation pressure

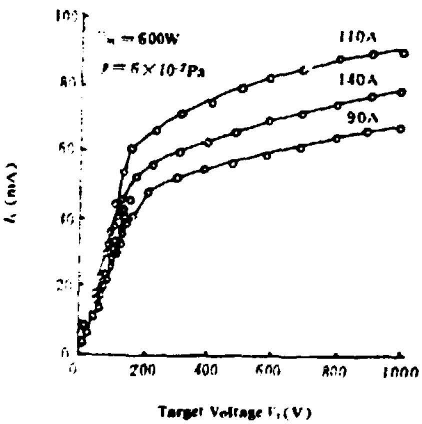

Fig. 5 Relationship between target current and voltage for several magnet coil's current

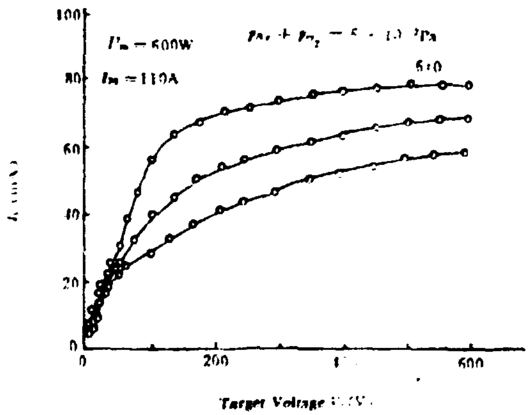

Fig. 6 Relationship between target current and voltage for several the ratio of p_{Ar} to p_{O_2}

3.2 Selection of V_t and V_s

V_t has great influences on the properties of superconducting film, because the superconducting material target has three ingredients (Y, Ba, Cu), with different sputtering yields at the same target voltage. When V_t is changed, the ratio of sputtering yields of three ingredients also has to be changed. We utilize this principle to control the ratio of three ingredients to be deposited on the substrates.

A self-floating potential V_f can be generated on the substrate[11]. In the experiment of deposition Y-Ba-Cu-O superconducting film, we selected V_f as substrate bias, which, on the one hand, is profitable for enhancing the adhension between film and substrate, on the other hand, is not enough to cause superconducting film re-sputtering.

3.3 Relationship between composition and gas atmosphere

The ratio of Y, Ba, Cu in superconducting film depending on the Ar partial pressure is shown in Fig. 7. For the lower Ar partial pressure, and more O_2, the more Cu atoms deposit on the substrates. However, with the increasing of Ar partial pressure, more and more Ba atoms have been deposited. it is clear that sutiable partial pressure of Ar and O_2 are needed.

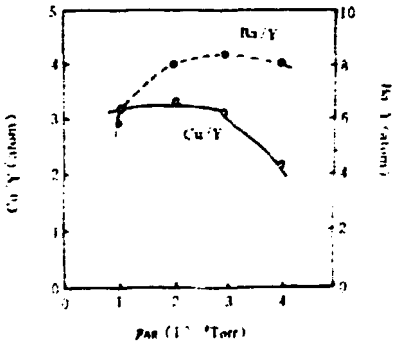

Fig. 7 Dependence of composition on gas atomosphere.
Where $p_t = 4 \times 10^{-2}$Pa

3.4 Distribution of composition with space location

The mean composition of the film does not depend on the distance between target and substrate, but the radial distribution of composition does. Properly select the distance, the radial non-uniformity of the composition could be less than 5%.

The experiments have demonstrated that the highest quality superconducting film could be deposited only at the optimum plasma parameters, which we have got are as follows: electron density N_e is about $1.5\times10^{12}cm^{-3}$; ionicity k, 25%; electron temperature T_e, 15 eV; the radial distribution of N_e is uniform. The experiments have also demonstrated that the optimum plasma parameters are corresponding to the optimum operating parameters as follows

P_m is 600 W; I_M, 150 A; p_{Ar}, 6×10^{-2}Pa; V_t, 600 V; V_f, -110 V.

The Y-Ba-Cu-O thin film deposited at the forementioned optimum parameters has a brownish-black, uniform and compact surface, and is amorphours shown by XRD pattern. Its thickness is about 1.0 μm. After a post-annealing at about 900℃ it turns to be superconducting and has a good c-axis orientation. After a post-annealing at 960℃ for 5 minutes, the superconducting transition of one sample is shows in Fig. 8. The dependence of resistance on temperature has been obtained by standard four-probe method. The temperature is measured by a calibrated copper-constantan thermal couple.

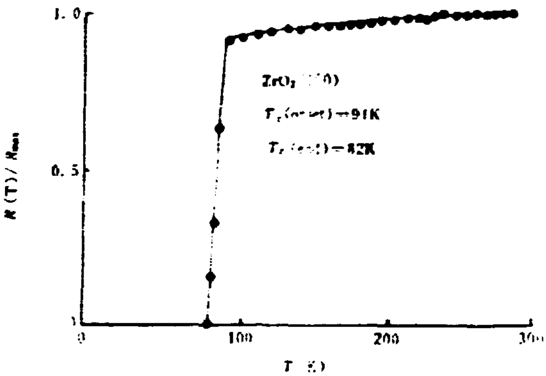

Fig. 8 Superconducting transition of sample

The XRD pattern shows that the sample have few secondary phases, one of them has 5(OOL) orientation, with $c = 1.175$ nm, $b - a = 0.007$ nm. All this means that the film is high Perovskit structure, which could be have high zero resistance temperature and critical current density. One of the best superconducting film has onset transition temperature 91 K and zero resistance temperature 82 K. This technique could be valuable for depositing superconducting film without post-annealing. Further work has been proceeding.

We emphasize that the depositing rate for superconducting film by this method is about 10.0 nm/min. It is four-five times the rate by RF discharge and is twice the rate by magatron sputtering.

4 SUMMARIZE

Many's the experimental results of coating film demonstrate completely that microwave ECR plasma deposition technique is aspecial coating technique, which has the advantage without compare with other vacuumcoating film as the fellowing:

(1) Lower Temperature Deposition Film

Lower temperature deposition film is especialy very important for microelectronics. It has became reality, because the ions are in the majority at the process of deposition film and have stronger reactivity than the atoms or molecules.

(2) Multiple Films

Various metal films and chemical compound films have been depositing. It is able to deposite defficult melting metal films, because a ion sputtering apparatus with high rate is set and fully oxide films or fluor-complex films, because ECR plasma is produced without any electrodes and is directly operated in many atmospheres of reactive gas, for example, O_2, F_2, N_2 and etc.

(3) High Quality Film

Various metal films and chemical compound films with a good compactness and a intensive adhesion can be deposited. The size of the crystal constructing of the film is about 10 nm. The adhesion is about 98 kPa.

(4) High Deposition Rate

The deposition rate is the highest at the ion sputtering, because the plasma has the highest density and the highest ionicity.

(5) Large Area Uniform Film

The uniform film at the 10 cm diameter can be deposited. In the area, nonuniformity of the film is about 5%.

(6) High Purity Film

It is able to deposit the highest purity films, because it has higher limite vacuum (10^{-6}Pa) and operate at lower pressure ($10^{-2} \sim 10^{-3}$Pa) without any electrodes.

In general, microwave ECR plasma is the best plasma source to apply to physical vapour deposition technique; microwave ECR plasma physical vapour deposition technique has wide application in the future.

The authors would like to thank, Sui Yifeng, Zhang Fengying for their contributions and encouragement.

REFERENCES

[1] Fu Liwen. Physics Monthly, 1989, 18(3)

[2] Huang Chaosong, Ren Zhaoxing, et al. Nuclear Fusion and Plasma physics, 1987, 7: 151

[3] Wen Haihu, Sheng Yanya, et al. Proceedings of international conference on the superconductor. Beijing, China, 1989.

[4] R. B. Laibowitz, R. H. Koch, et al. Phys Rev, 1987 B35: 8821

[5] P. Berberich, J. Tate, et al. Appl Phys Letts, 1988, 53: 925

[6] Cao Xiaowen, Wen Haihu, Zhang Fengying. Physics, Monthly, 1988, 17: 614

[7] S. Yukinori, S. Kazuhiko, et al. Jpn. J. Appl. Phys, 1988, 27: 1103

[8] J. J. Yeh, M. hong, R. J. Felder. Appl. Phys. Letts, 1989, 54: 1163

[9] J. Kwo, T. C. Hsieh, R. M. Fleming, et al. Phys. Rev, 1987, B36: 4036

[10] A. Inam, M. S. Hegde, X. D. Wu, et al. Appl. Phys. Letts, 1988, 53: 908

[11] Seito Matsuo, Mikiho Kiuchi. Jpn. J. Appl. Phys, 1983, 22: 210

微波 ECR 等离子体物理汽相沉积研究和应用

原子能出版社出版

（北京 2108 信箱）

原子能出版社激光照排中心排版

北京市海淀区三环快速印刷厂印刷

☆

开本 787×1092 1/16 · 印张 1/2 · 字数 12 千字

1991 年 6 月北京第一版 · 1991 年 6 月北京第一次印刷

ISBN 7-5022-0514-1

TL · 277

CHINA NUCLEAR SCIENCE & TECHNOLOGY REPORT

ISBN 7-5022-0514-4
TL・277

P.O.Box 2103
Beijing, China

China Nuclear Information Centre