NEW APPLICATIONS OF R.F. PLASMA TO MATERIALS PROCESSING

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ABSTRACT

An RF inductively coupled plasma (ICP) torch has been developed as a typical thermal plasma generator and reactor. It has been applied to various materials processings such as plasma flash evaporation, thermal plasma CVD, plasma spraying, and plasma waste disposal. The RF ICP reactor has been generally operated under one atmospheric pressure. Lately the characteristics of low pressure RF ICP is attracting a great deal of attention in the field of plasma application. In our researches of RF plasma applications, low pressure RF ICP is mainly used. In many cases, the plasma generated by the ICP torch under low pressure seems to be rather capacitive, but high density ICP can be easily generated by our RF plasma torch with 3 turns coil and a suitable maching circuiit, using 13.56 MHz RF generator. Plasma surface modification (surface hardening by plasma nitriding and plasma carbo-nitriding), plasma synthesis of AlN, and plasma CVD of BN, B–C–N compound and diamond were practiced by using low pressure RF plasma, and the effects of negative and positive bias voltage impression to the substrate on surface modification and CVD were investigated in details. Only a part of the interesting results obtained is reported in this paper.

INTRODUCTION

Thermal plasma used for materials processing is mainly generated by using a DC plasma torch. Thermal plasma also can be simply generated by using AC arc discharge. Besides the DC plasma torch, another typical equipment to generate thermal plasma for materials processing is an RF inductively coupled plasma (ICP) torch. A new type of plasma torch called "hybrid plasma torch", which is consisted of the DC plasma torch and the RF plasma torch, has been commercially developed[1].

Typical processes using RF inductive ther-mal plasma are ICP chemical analysis, plasma spraying, plasma flash evaporation, thermal plasma CVD and plasma disposal of wastes. Plasma flash evaporation process is consisted of evaporation of solid particles of raw materials and condensation of solid film or particles as final product from vapor of the materials. It was successfully applied to deposit YBCO and BSCCO film with very im-proved superconducting properties[2,3]. The hybrid plasma torch was also successfully ap-plied to high rate thermal plasma CVD of ce-ramic materials such as SiC and Si_3N_4[4].

These thermal plasma processes are often practiced under reduced pressures. ICP under

low pressures deviates from thermal equilibr-xiumstate and its application to the deposition of c-BN is noticeable[5-7].

Lately helicon plasma generated under low pressure (0.1-10Pa) using RF discharge with impression of parallel magnetic field is notice as a high density plasma. Such highly ionized state can be also obtained in a low pressure RF inductively coupled plasma without any application of magnetic field.

In our plasma application researches at Science University of Tokyo, RF inductive plasma under low pressure was applied to surface hardening of metals (nitriding and carbo-nitriding), surface modification of substrate for CVD of high quality diamond, rapid synthesis of metal nitrides (AlN, Mg_2N_3), and CVD of BN (c-BN) and B-N-C compound.

Generally the plasma used by us is not always high density RF inductive plasma, although the plasma is generated in quartz tube by using an RF inductive coil. In some cases, the characteristic of the plasma was rather capacitive, but in almost cases, the d.c. or r.f. bias voltage was impressed to the metal or the substrate. Very interesting phenomena, such as promotion of plasma surface reaction at low temperatures and change of microstructure of deposit or modified layer, were observed by such bias impression.

We also found that high density plasma under low pressure can be generated by using 13.56 MHz RF generator in a long cylindrical quartz chamber with a modified matching circuit, 3 turns of inductive coil. High density nitrogen plasma was also applied to nitriding process and the effect of ion flux on nitriding was investigated. The result obta-ined by such high density plasma was analyzed, compared with that by low pressure RF plasma.

The survey of RF inductive thermal plasma applications to materials processings and the results of our RF plasma applications will be reported here.

EXPERIMENTAL PROCEDURE

One example of our RF inductive plasma torches are shown in Fig.1(A), (B). The inner diameter of water-cooled quartz tube is about 40-50mm and its length is devided, according to the sort of experiment. RF (4 or 13.56Mhz, 5-10kW : plate power of RF generator) is generally supplied to plasma from a three-turns Cu coil wound outside the quartz tube. Various gases of commercial grade are supplied to the torch as plasma forming gases and reactants. In some cases, high grade gases, for example, for semiconductor processings, are used. The plasma is formed in the quartz tube under reduced pressure (1 $\sim 10^{-2}$ Torr). The substrates(specimen) holder which is made of ceramic material such as BN includes a nichrome wire heater and a metal electrode (Cu electrode in this figure). The temperature of the substrate is measured by a thermocouple in contact with the back of the substrate and regulated to indicate a desired constant value during the experiment. The substrate potential can be negatively or positively biased and kept at a constant value by applying DC or RF power to the electrode to control the energy of ion bombardment to the substrate. The biased potential Surface
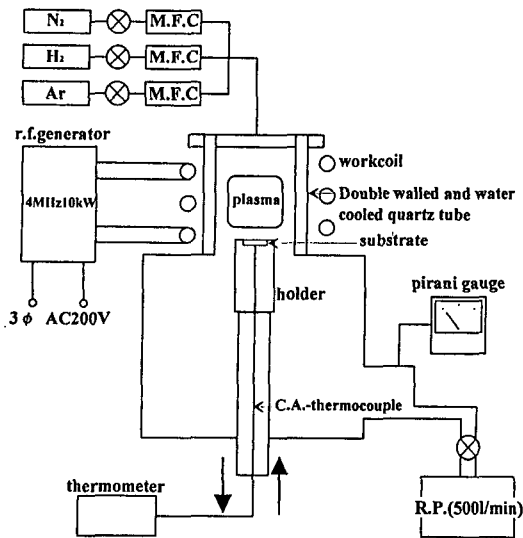
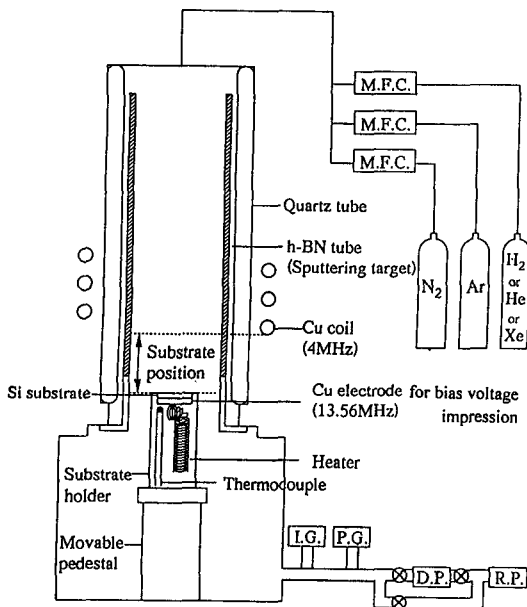Fig. 1A Apparatus for RF plasma processing
(A type)

Fig. 1B Apparatus for RF plasma processing
(B type)

hardening by plasmacan be meeasured as the difference between the substrate potential and the ground potential (0V) by a VDC meter in the case of RF power supply.

RESULT AND DISCUSSION

nitriding and plasma carbo-nitriding

(1) Plasma nitriding of iron and stainless steel

The sample(substrate) of iron (size: $1mm \times 10mm \times 20mm$, purity: 99.96%) or SUS-304 steel (size: $2mm \times 10mm \times 20mm$) was polished to obtain a miller-like surface and washed in acetone by supersonic wave. Then the sample was heated in H_2-Ar RF glow plasma (H_2/Ar=90sccm/10sccm, 823K) to clean and activate its surface and after that pretreatment, it was treated in N_2-H_2 RF plasma (N_2/H_2=90sccm/10sccm). In this treatment, DC bias voltages ranging from +50V to -200V were imposed to the sample, using a closed circuit asshown in Fig. 2. The temperature of the sample was fixed at 823K and the pressure in the reaction chamber was maintained ca. 32Pa.
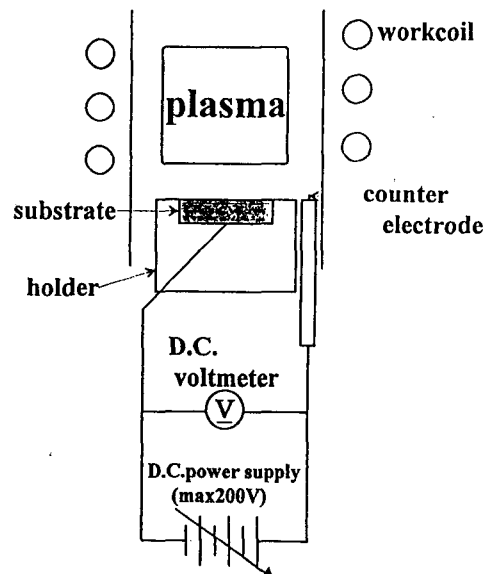

Fig.2 D.C. circuit imposing bias voltage
to the substrate

Nitriding of iron and SUS-304 under pure RF nnitrogen plasma was reported in detail by us[8]. The results were arialyzed and compared with those in DC ion nitriding reported in the past[9].

In the plasma nitriding (ion nitriding) using DC glow plasma where the sample is used as a cathode, hydrogen is often added to nitrogenm Because hydrogen can check the oxidation of the sample by a small amount of oxygen to be included in plasma atmosphere. But, in such RF plasma nitriding of iron, the prevention of nitriding by the addition of hydrogen was first-observed by Matsumoto[10] and secondly confirmed by[8].

The results in our nitriding experiments of iron for 120min in the N_2-H_2 RF plasma are summarized as shown in Fig. 3. Here bias voltage 0 means that the sample is placed in the plasma without bias voltage impression. So the sample is in a floating state. Of course

Fig. 3 Thickness of nirided layer, compound layer and denitrification layer v.s.D.C. bias voltage to the specimen
(Substrate:Fe N_2:H_2=90:10 550℃ 120min)

some negative self-bias potential, comparing with the plasma potential, is impressed to the sample in this case. The front of nitrogen invasion (diffusion) into iron can be clearly observed in the microphotography by metallographic microscope, because the microstructure of virgin sample phase is quite different from that of nitrogen including phase. Accordingly, both phases can be clearly distinguished. We call this nitrogen including phase "nitrided layer". The surface layer without nitrogen(α-iron layer) is often observed. We call such surface layer "denitrification layer". A compound phase (γ phase:Fe_4N) can be formed by nitriding of iron in nitrogen plasma. The layer consisted of this compound also can be clearly distinguished from another layer (α-iron or nitrided layer). We call this layer "compound layer". When the bias voltage ranged between 50V and -50V, denitrificaion layer appeared, but the thickness of nitrided layer became larger, with the shift of bias voltage from -200V to 0V. The denitrification layer was not observed with the shift from -200V to -100V, but it appeared and its thickness increased with the shift from -50V to 50V. These results suggest that the negative bias voltage impression to the sample promotes the formation of compound layer and prevents the for matioin of denitrification layer with increase of high energy flux of incident nitrogen ions to the surface. However, the diffusion of nitrogen into the sample from its surface, is retarded by the growth of compound layer, therefore the thickness of nitrided layer decreases with the shift of bias voltage from -200V to +50V. Such phenomena means that nitriding of iron is controllable with the im-
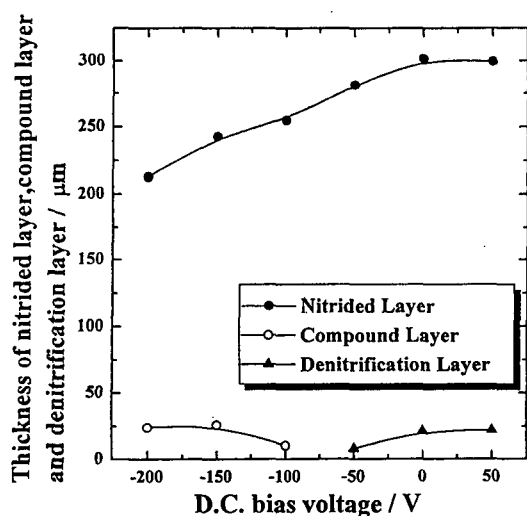
pression of bias voltage to the sample under the presence of RF plasma as nitrogen ions and radicals source.

The ,nitriding of SUS-304 sample using pure nitrogen RF plasma, was also remarkably promoted with the negative DC bias voltage impression. The hardness(Hv) of surface nitrided layer reached about 1000, as shown in Fig.4. In the sample treated at higher negative bias voltage, the hardness of the surface is somewhat lower than that of inner part of the sample. It is possible that nitrogen content in the surface layer decreases with the increase of negative bias voltage.
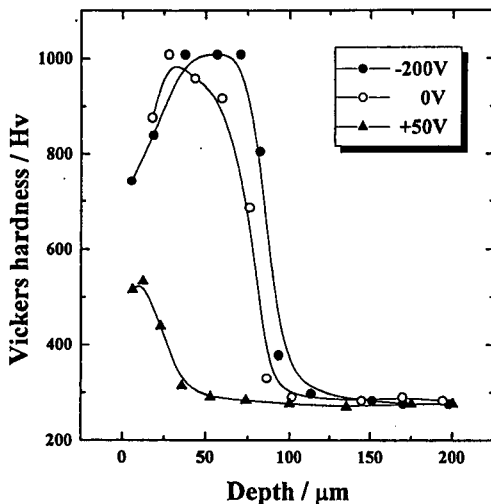

Fig. 4 Microhardness v.s. the distance from the surface at different bias voltages impression(substrate:SUS304 N_2:H=100:0 550 ℃ 120min)

(2) Plasma nitriding and carbonitriding of titanium

Our reports of RF plasma nitriding of Ti alloy (Ti-6Al-4V) were published in 1992 and 1993[11, 12].

RF plasma nitriding of pure Ti sample (purity : 99.5%,   dimension : $10 \times 20 \times 1mm$)after

the pretreatment as described in 1-(1) was carried out for 20～240 min at different temperatures(1030～1373K), 1.0～1.3 Torr in pure nitrogen or mixture of nitrogen and hydrogen (hydrogen content : 10%). The RF power in putwas '1.2～1.5kW. The addition of hydrogen to nitrogen increased nitroding rate and hardness of nitrogen diffusion layer. Kinetic study indicated nitriding behavior changed in the temperature range 1273K and 1373K. It is considered that ε phase, which has the effect of suppressing nitrogen diffusion, disappears in the sample nitrided at 1373K. The nitriding rate decreased in the samples with a positively d.c. biased potential. It is therefore probable nitrogen ions exerted some effect on the nitriding rate. The nitrogen diffusion layer formed by the plasma nitriding was harder than that formed by thermal nitriding. Hence, nitrogen concentration in the nitrided layer of the plasma nitrided sample must be higher than that in the thermal nitrided sample.

In the plasma nitriding of Ti-6Al-4V alloy, the sample (dimension : $10 \times 10 \times 1mm$) was generally maintained in an electrically floating state in the RF plasma generated uaing pure nitrogen-hydrogen mixture. Nitriding conditions are as follws ; Total pressure : 200 Pa, Total gas flow rate : 120～180 sccm, Nitriding time : 10～300 min, Treatment temperature : 1070～1370 K, H_2 concentration : 0～50 vol%, DC bias voltage : -250～+250 V. By addition of hydrogen into nitrogen, the nitriding rate was promoted and δ-TiN phase was preferentially formed at relatively lower temperatures. It is probable that active ions and N-H radicals in the plasma can attribute to such phenomena.

According to SEM observation, it was made clear that the change of the nitrided surface morphology becam more remarkable with the elapsed nitriding time and the increase of hydrogen content in the gas mixture. We also attempted to impose a DC bias voltage to the alloy sample in the RF plasma. The promotion of nitriding and other interesting phenomena such as phase transition from ε to δ and increase of surface hardness, were observed in such RF plasma nitriding assisted by charged particles bombardment on the negatively biased sample. Fig. 5 shows the tendency of change of nitrided layer thickmess with the change of Dc bias voltage. Thermal nitriding of the sample without plasma was tried to confirm the diference between characteristics of plasma nitriding and thermal nitriding. Especially the nitriding rate in RF plasma was much larger, compared with that in thermal nitrogen atmosphere.
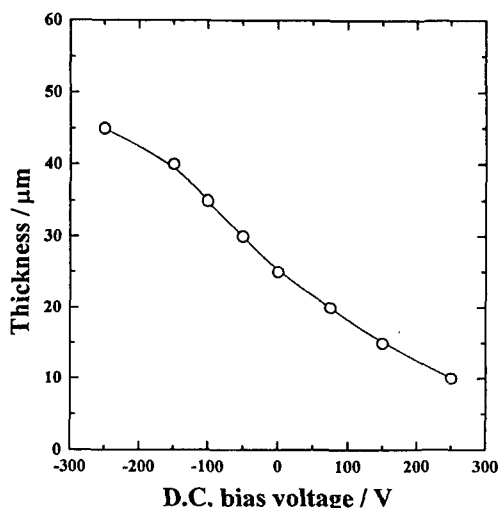

Fig. 5 Thickness of nirided layer v.s. D.C. bias voltage to the specimen
$(N_2:H_2) = 90:10$ 1270K 120min)

Plasma carbonitriding of Ti sample (dimension : same as that in the experiments described above) was the DC bias impression to the sample. Here the mixture of nitrogen and acetylene $(N_2:C_2H_2=90:10, N_2:C_2H_2=99:1)$ was used as reactant gas. Thick and hard Ti (C, N) layer was successfully and rapidly formed at rather low temperatures with the negative bias voltage impression to the sample. However, the carbonitriding behavior was strongly on carbon concentration in the atmosphere. The carbonitriding was promoted even in the case of low content of carbon in the gas mixture with negative bias impression to the sample. The details of the results have been reported in our paper[13].

Diamond deposition on titanium and iron samples preteated in N_2-C_2H_2 plasma

High quality diamond film was successfully deposited on titanium and iron samples pretreated in nitrogen-acetylene RF plasma. Combusion flame method using acetylene and oxygen was used for deposition of diamond film, because the deposition rate is very fast in this method. The details of the results have been reported in our paper[14, 15].

Plasma nitriding of aluminum

The nitriding reaction of aluminum sample proceeded rapidly in RF nitrogen plasma under low pressure. When thick alumimun plate (thickness : several mm) was used, the reaction finished in a few minutes, without melting of Al, and pure AlN sample was obtained. The control of the reaction was rather difficult, because the reaction was exothermic. Now we are trying to obtain dence, thick and sintered nitride surface layer of alumi-

num by the careful control of plasma condit-ions. A part of our experimental results has published in the proceedings of ISPC (International Symposium on Plasma Chemistry)[16].

BN and B-C-N compound deposition by Plasma CVD

BN deposition by sputtering of h-BN target using RF ICP was tried. The target is consisted of h-BN tube which is inserted in a quartz tube. The RF plasma is generated in the h-BN tube and wall of the tube is sputtered. By such new method, high-quality h-BN film was deposited on Si wafer of semiconductor grade.The details of the results were reported in the proceedings of ISPC[17].

Plasma deposition of BN using solid boron particles as boron source, hydrogen and nitrogen as reactant gases was carried out at low pressures. Cubic BN (c-BN) thin film including some amount of h-BN was prepared by controlling the substrate (Si wafer) potential and H_2/N_2 flow ratio in the plasma. In this process, it is not necessary to use dangerous raw materials such as boron hydrides or organic boron adducts which contaminate the film. We found that 1073K was the most suit-able substrate temperature for c-BN growth in our exeriment. The hydrogen content in the plasma must be as low as possible with a suitable bias voltage impression to the subst-rate for c-BN deposition, because energetic hydrogen ions have the possibility of chemically interrupting the formation of c-BN and sputtered etching of BN deposit. The details of the results were reported in our two paper[18, 19].

Preparation of BN by plasma MOCVD using trimethyamine-borane as boron source was carried out using low pressure RF p

lasma. This material is of safety and easy to handle. In this study, the total pressure of H_2 and N_2(Volume ratio : 100/0~0/100) and RF power input were maintained at 110 Pa and 4kW, respectively. The evaporator temperature of boron source was maintained at 353K. The ratio of B/N in the deposited film deposited on appropriate position in plasma was about 1/1, but a lot of carbon was included in the film. We are continuing the experiments to estimate the bonding states of carbon and compare the states with those of films prepared by thermal CVD. Preliminary experimental   re   -
sults have been reported at Gordon Conference of Plasma Science and Technology held in New Hampshire, U.S., this year.

Transparent and smooth films consisted of sp_2-bonded turbostratic BN were obtained by thermal plasma CVD using an RF inductive plasma torch and $Ar-BF_3-N_2$ ($-NF_3$) gas[20].

High density RF inductive plasmaand its applications

This plasma can be generated under low pressures (several Pa). Such type of plasma is being successfully applied to plasma etching process in the fabrication of semiconductor devices, but few reports of other applications have been published. We have succeeded in generation of such plasma by RF inductive technique using 13.56MHz plasma generator and a suitable RF coil. We are trying to apply such plasma to CVD process such as MOCVD of boron and surface modification of metals.

CONCLUSIONS

The importance of bias voltage impression to the substrate (metal) in RF inductive plasma processes such as plasma surface modification and plasma CVD has been made clear in our experiments. It is particularly interesting that surface reaction in surface modifiication can be remarkably promoted. Furthermore, it was confirmed that low pressure high density inductive plasma can be easily generated by using 13.56MHz RF generator, appropriate matching circuit and RF coil. The applications of such high density plasma to various surface treatment processes must be actively studied.

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