THE APPLICATION OF THE PLASMA CHEMICAL REACTION IN THE R.F ION SOURCE

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Abstract

The paper introduced a cross science of the chemistry and the physics -- the technique of the plasma chemical reaction in applying the r.f ion source. By this technique, the problem of drawing metal ions were solved. especially, the problem of drawing the high volatilize temperature metal ions were solved. The ions drawn are: Re^+, W^+, Mo^+, Pd^+, Pt^+, Ta^+, Au^+, Ag^+, Ti^+, Cr^+, V^+, Fe^+, Cu^+, Si^+, Al^+, Mg^+, Be^+, Ga^+, In^+, Bi^+, Li^+, and the drawn ions of the rare earth element are: Y^+, Ce^+, $Nd^+$and so on. The technique has been used for five years in a 400Kev ion implenter in Beijing Normal University, good result has been obtained.

1. Foreword

The work of the past in r.f ion source had been reported.[1][2] This paper is mainly recounted a cross discipline of the chemistry and the physics -- The technique of the plasma chemistry reaction in applying the r.f ion source. By this technique, the problem of drawing metal ions were solved, especially, the problem of drawing high volatilize temperature and chemical property steady metal ions were solved.

2. The experimental structure and the principle

2. 1 The experimental structure

In Fig.1 the sketch structure of the r.f ion source is shown. 1 - 1 is the discharge chamber from the quartz glass. 1 - 2 is the desired metal of producing ion, and the kind of the metal is are changed according to the requirement, the part that is unwanted to produce chemical reaction is shielded by a quartz glass tube which interior diameter is ϕ4mm. 1 - 3 is the shield cover from the quartz glass, provides with a ϕ5mm hole at the centre. 1 - 4 is the extracting electrode which is 8mm long and with a 5mm outer diameter and 2.5mm inner diameter. There are a gap between its upper face and the quartz shield. 1- 5 is the flange through which the gas enters into the disharge chamber. 1- 6 is the extracting electric source, forming a potential difference the andode (1 - 8) and the cathode (the extracting electrode), and the votage can be adjusted continuously at a range 0 -- 5Kv. 1 - 7 is the coil of the r.f oscilletor, it is horizontally installed, of course, can also be vertically sheathed to the outer discharge chamber. 1 - 9 is the assistant power supply, it is made for producing a negtive potential in the reaction matter relotive to plasma (anode potential) in a centain condition, for some elements it is used when the sputtering voltage needs to be added. 1 - 10 is furgus form connection for the convenient change of the reaction matter and the anode at the same time it can be used for keeping vacuum.

2.2 The working principle

According to the characteristic of the r.f ion source with a discharge chamber made of quartz glass, by meas of the phsical and the chemical method a plasma which contain the halogen formily element and the metal element for producing required ion in the discharge chamber is formed, then by the drawing system of the source and the magnet anelyser metal ion needed is obtained.

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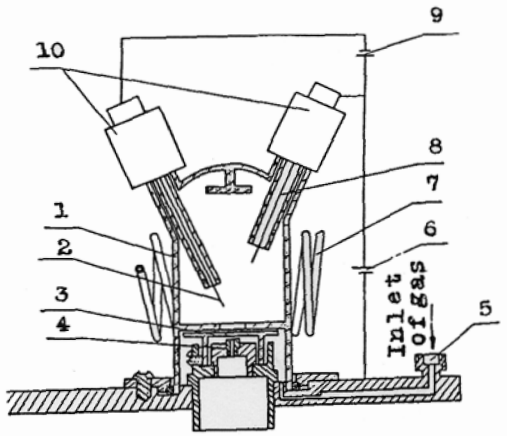

Fig. 1 The structure of the r.f ion source by the use of plasma chemistry reaction.

For this purpose, firstly the halogen family element is transported pass through falange of feeding gas into the discharge chamber made of quartz glass, and the gas is ionized by the coil of the r.f oscillator, the plasma of the halogen family element is produced. Then the halogen element and the ions of the halogen element chemically react with the metal for producing wanted ions, the plasma containing both halogen ions and metal ions is further formed. For this plasma, its dynamic equilibrium of the combination (synthesize) and the resolution, the excitation and deexcitation, the ionization and the recombination, the gas feed and the exhaust and the other processed must be maintained, particles of varied states are present at some time, various prosessed are proceeding simultaneously and the stabilit is over a long time, but is not a single direction change (e. g. to synthesize only certain production or in oppacition)

There are many favourable factors of this plasma which can be utilized, specially the high — energy particles and activeted particles.

(1) The electrons which constitute about one half of the amount of charged particles in plasma is must active in all particles. They have higher energy, ranged 1 - 10 ev.[3] For such high energy, generally by the heating method is difficult to reach. The electrons is the major transmitter (or transporter) of the energy. It make the energy of electromagnetic field be transformed to kinetic energy of the particles, the heat energy, the light energy in discharge chamber. Because the electrons have higher energy, it lead to a resolution of the moleculera, a activation and a ionization of the atoms and the moleculers and so on, as they collision with the particles.

(2) The gas moleculers and the compounds of the halogen family elements are resolved easily in the process of their collision with particles (bombarded by particles) in plasma. When the moleculers of the halogen family are resolved, they will absorb energy.

For example: $Br_2 \xrightarrow{1.97ev} Br+Br$

$Cl_2 \xrightarrow{2.48ev} Cl+Cl$

For two Bromine atoms the energy increase 1.97ev more than for one molecule (Br_2) For two chlorine atoms the energy increase 2.48ev more than for a molecule (Cl_2). The clemical nature of atoms is more active than that of molecules.

(3) The atoms of the halogen is ionized into ions and electrons in the plasma. In this process, a port of energy is increased again.

For example: $Br \xrightarrow{11.8ev} Br^+ + e$

$Cl \xrightarrow{13ev} Cl^+ + e$

A Bromine atome is ionized into a ion (Br^+) and an electron (e), the energy is increased by 11.8ev, while two atoms (be a molecule) are ionized into two ions and two electrons, the energy are increased by 23.6ev + 1.97ev = 25.57ev.

For the same reason a molecule (Cl_2) is ionized into two ions and two electrons, the energy are increased by 28.48 ev.

The ability of the ion acquiring electrons are stronger than that of molecule and atom, it is more easily for the chemical reaction with the metal to take place. The fact that ions join chemical reaction is a important characteristic of chemical reaction of the plasma. In the process of the ions of the halogen colliding (or the contacting) with the neutral atoms of the metal each other, the ions of the halogen can capture the outer electrons of the metal (or called charge transfer), making metal atom into ion.

Such as: $Re + Cl^+ \text{ ---- } Re^+ + Cl$

$W + Cl^+ \text{ ---- } W^+ + Cl$

$Pd + Br^+ \text{ ---- } Pd^+ + Br$

This process is easily performed, because three elements (F, Cl, Br) used in reality, have the ionization energy of more than 11ev, while the ionization energy of all metals in the periodic table are under 10.6ev.

(4) There are much atoms in excited state in the plasma in the discharge chamber and their chemical character are very vivid. for chemical reaction easily taking place. As is known to all from the plasma light a large number of the particles are in excited. The light is given out mainly in the process at wlich the outer electrons of the excited state particles jump to a lower energy level from a higher one. So long as the plasma not goes out, it indicates that a great quantity of the excited state particles are present. The excited atoms (or molecules) also possess more energy than the not excited ones. It can be calculeted from formule

$$\varepsilon = h\frac{c}{\lambda} = h\gamma$$

Such as: Ta^*(excited state) 2.6ev
energy more than Ta

Pd^*(excited state) 3.44ev
energy more than Pd.

(5) The chemical reaction is more easy to occur[4,5] between the positive ions and the negative ions in the plasma. Because it is a non solvent reaction, in which the two reactionts opposited charged are not keep aparte by the solution, the attracting electromagnetic force between the positive ions and the negative ions is larger and the positive ions and the negative ions are "nude" reactive metter, which can react directly, the reaction is extremely rapid.

(6) Part of the light energy in the plasma can be used. In all processes that the electrons in outer space of the excited state atoms (or molecules) from a higher energy level jump to a lower one; the positive ions recombinate with the negative ions and the electrons recombinate with ions, ect, photons will be emitted, these photons will be absorbed easily by the corresponding particles and the substances and new excitation will be given, rise and so on.

e.g: Re $\xrightarrow{4489A^\circ \text{ wave longth}}$ Re*

Pd $\xrightarrow{3634A^\circ \text{ wave longth}}$ Pd*

Partial surface of the metal reactant accepts being plasma light, it makes part of photon energy being used.

(7) The duo-pole diffuse effect[6] is an inherent physical characteristic at the boundary between the plasma and the metal. Owing to this nature, the much ions and the electrons flow to the surface of the metal from the plasma. So, (a) An amount of the halogen contaction with the metal is increased; (b) thus particles have definite energy. As a result of the effect, the physical and the chemical sputtering are inevitably present.

Above mentioned factors and other beneficial factors existed in the plasma, make the compound being easily formed between the halogen element with metal. These compounds are easy to be evaporated, resolved, ionized, and various processes are instantaneous and continuous, it provides with favourable condition to extract metal ion.

In addition to the inherent favourable factors in plasma are utilized, more advantageous conditions have been created.

(1) 1 - 2 and 1 - 8 are replaced by the metal for producing needed ions. For certain elements, The extracting electrode are replaced by the metal for producing required ions too.

(2) A voltage is added between the plasma (anode) and 1 - 2 (the metal for producing needed ions) by 1 - 9 (the power), then 1- 2 is at negtive potential. The potential differance can be adjusted in a range 0 -- 5Kv, a large number of charged particles with thousends electron volt energy are give rise to, thus more higher energy positive ions with the halogen family element are formed compelled to shoot to 1 - 2 and the extracting electrode (cathode), however, the electrons and the negative ions

shoot to anode.

On the one hand, the contaction number between the halogen element with the metal is much more increased, on the other hand, the high -- energy particles bombard metals to heat metals and make the bond break between atoms and atoms of the metal, therefore the chemical reaction speeds up. The halogenide of the metal is sputtered, volatilized , resolved, ionized immediately owing to the raised temperature and successive bombard by the particles. After this measure has been taken, the ion beam of metal (e.g. Ta, Pt, Cr, ect.), that is difficultly to get in genaral condition, is conveniently obtained. Simultaneously the percentage of the metal ion in total beam is rised.

The method of the ion bombardment can be applied to high melten point metals. For low melten point metals the sputter voltage is not applied, but metals is put in a boat made of quartz which is placed in discharge chamber.

3. The experimental results and their use

3.1 The experimental results at the ion source bench

By the use of this technique, the ions drawn at the ion source bench are: Re^+, W^+, Mo^+, Pd^+, Pt^+, Ta^+, Au^+, Ag^+, Ti^+, Cr^+, V^+, Fe^+, Cu^+, Si^+, Al^+, Be^+, Mg^+, Ga^+, In^+, Bi^+ and Li^+, and the drawn ions of the rare earth elements are: Y^+, Ce^+, Nd^+, and so on.

Graphs shown in Fig.2 to Fig.5 are the ion mass spectrum of Ta, Pd, V, Cr and some other elements respectively after a plasma chemical reaction with the halogen family elements.

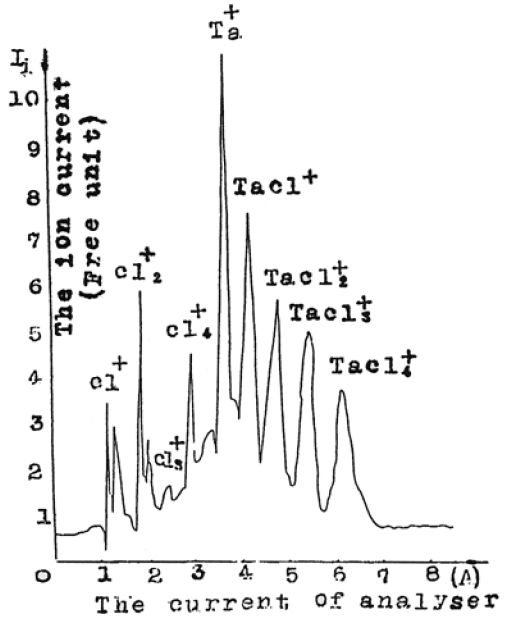

Fig.2 The ion mass spectrum of Ta + CCl_4.

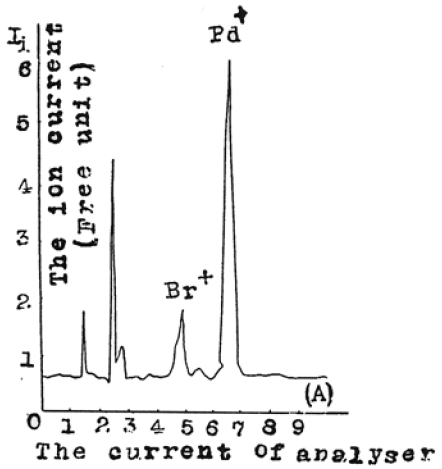

Fig.3 The ion mass spectrum of Pd + BBr_3.

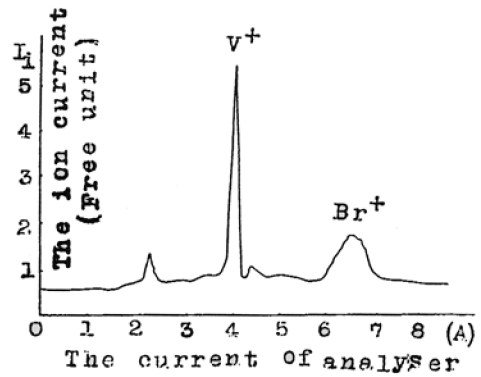

Fig.4 The ion mass spectrum of V + BBr_3.

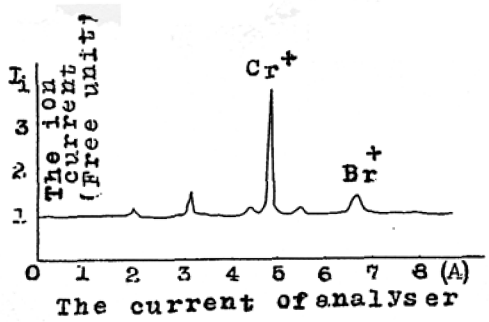

Fig.5 The ion mass spectrum of Cr + BBr_3.

3.2 Used cases at ion implanter

This technique have been used at a 400kev ion implanter in Beijing normal university for several years. It is stable in operating and becomes a ripe technology. Part of the results for the ion current intensity at the target after passing through the magnet analyser were list in the table, for some kind of ions good results have been obtained.

The table of ion current intensity of part metals at the target in a 400kev ion implanter

Ions :	Ti^+	Pd^+	Ga^{69+}	Ga^{71+}	Bi^+	In^+
Ion current intensity(A):	100	120	50	33	85	300
	Fe^{56+}	Fe^{57+}	Be^+	Li^7	Li^6	Ta^+	Y^+
	54	2	150	130	3	12	30

4. Concluding remarks

By applying a across science of the physics and the chemistry ___ the plasma chemical reaction technique, to draw metal ion beams from a r.f ion source, the problem of drawing ions of metals with higher volatization temperature are solved. It has its own merit. Since it used quartz glass discharge chamber, the chemical property of the quartz glass is more ateady than that of metals, the metals that is no need to produce ions can be shielded and can not be exposed to plasma, then useful metal ion content is higher in the draw ion beam. The noble metals which are not exhausted in one time can be used continuously in next time. It is no need to compose metals into compounds before putting them in discharge chamber. For this reasion, it has advantages of simplicity the convenience and the economy. This technology can be used at ordinary ion implanters and accelerators with r.f ion source, provided some improvement of these machines is made, so as to expend the usage and bring into full play of the machines and raise the economic benefit.

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