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doi:10.15199/48.2016.08.43

Production of rare earths ion beams in arc discharge ion source using their oxides

Abstract. *Production of rare earth's ions from using their oxides and carbon tetrachloride (CCl_4) vapor is described. Mechanism of internal chemical synthesis of rare earth's chlorides is proposed. Working characteristics like dependences of ion currents on discharge and filament current, magnetic flux density as well as CCl_4 flux are presented and discussed in order to find optimal working parameters. The separated currents of 18 μA, 5 μA, 3 μA and 12 μA were obtained for Eu^+, Gd^+, Ho^+ and Pr^+, respectively.*

Streszczenie. *W atykule opisana jest metoda wytwarzania wiązek jonów pierwiastków ziem rzadkich wykorzystująca ich tlenki i pary czterochlorku węgla (CCl_4). Zaproponowano także wyjaśnienie mechanizmu wewnętrznej syntezy chlorków ziem rzadkich. Celem znalezienia optymalnych parametrów pracy rozpatrywanane są charakterystyki robocze źródła, takie jak zależności natężenia prądów jonowych od natężeń prądu wyładowania, grzania katody, indukcji magnetycznej zewnętrznego magnesu jak również nacieku CCl_4. Otrzymano rozseparowane wiązki jonów Eu^+, Gd^+, Ho^+ i Pr^+ o natężeniach odpowiednio 18 μA, 5 μA, 3 μA i 12 μA. (**Wytwarzanie wiązek jonów ziem rzadkich z wykorzystaniem ich tlenków**).*

Keywords: ion sources, ion implantation, rare earths.
Słowa kluczowe: źródła jonów, implantacja jonowa, pierwiastki ziem rzadkich.

Introduction

Ion implantation is one of the most popular methods of material properties modification, e.g. is widely used in semiconductor industry, but could be also useful for the modification of tribological properties of solids [1], improving their chemical resistance [2], formation of nanostructures [3, 4] in semiconductors or polymers [5]. In order to cope with the diversity of needs, a variety of ion source designs as well as ion beam production procedures are developed [6, 7].

Rare earths are widely used in automotive and power industries as well as in microelectronics. Doping with rare earths modifies both tribological and magnetic properties (when Nd, Tb or Dy doping is applied). This property found application in preparation of permanent magnets used e.g. in wind power plants. In optoelectronics rare earths are used for modification of optical properties of active layers [8-10]. The first silicon based switchable two-colour LED diode was prepared by Eu doping of a silicon dioxide layer [11]. Especially in the later case the precise doping was crucial for obtaining the desired properties of modified layer. Thus, ion implantation in the only method that allows precise control of both the dopand dose and its range. The most popular ion sources used in implanters require either gas feeding, or substances with low melting point (Ga, In) or relatively high vapour pressure at low temperature (like $TiCl_4$). The lack of such compounds in the case of rare earths is a challenge ion source design and optimisation.

An efficient but rather power-consuming method of rare earth ion beam production is application MEVVA type ion sources [12]. It is also possible to use liquid metal ion sources and alloys of rare earths and other metals, characterised by lower melting point than pure rare earth (e.g. 765°C for Er-Ni [13] or 860°C for quarternary alloy $Er_{70}Fe_{22}Cr_5Ni_3$ [14]). Extracted ion currents are less than 1 mA, which may be to low for implantation purposes. Another solution is placing a container with rare earth feeding material inside the ion source and heating it with an intense electron beam [15]. Also the authors of the current paper proposed original method for rare earth beam production from their chlorides employing plasma ion source with an internal crucible heated by the discharge burning between anode and cathode filament [16]. Rare earth chlorides have melting points much lower than the pure rare earths (e.g. Eu_2Cl_3 decomposes at 632°C). In order to prevent the production of oxychlorides an additional leak of H_2 (~10 mbar cm3 / s) was applied. It should be mentioned that rare earth chlorides are highly hygroscopic – e.g. europium(III) chloride forms europium(III) chloride hexahydrate (characterised by melting point of 850°C) after even short exposure on humid air.

The paper presents new method of rare earths ion beam production using its oxides as the feeding substances. The crucial point of the method is application of carbon tetrachloride (CCl_4) vapours as a highly reactive carrier gas. This approach has been also successfully applied for molybdenum ion beam production [17]. A very similar method has been applied in the case of microwave ion source [18] in order to produce intense Fe^+ beam from hematite (Fe_2O_3). The paper contains a brief description of the ion source, experimental set-up as well as ion beam production procedures. The described method was tested using europium (Eu_2O_3), gadolinum (Gd_2O_3), holmium (Ho_2O_3) and praseodymium (Pr_2O_3) oxides. Dependences of the extracted ion current and discharge voltage on the discharge and filament currents are presented and discussed in order to find the optimal working parameters. The influence of magnetic field flux density of the ion source electromagnet is also investigated.

Experimental

The plasma ion source used for rare earths ion production was described in details in [19-21]. It is a modified version of Nielsen ion source. Schematic view of the device is shown in Figure 1. Cylindrical anode and front and rear cathode mounts (caps) are made of molybdenum (any other refractive metal could be also used) and form a plasma chamber of the ion source of the length ~20 mm and internal diameter of ~16 mm. The anode and cathode mounts are separated by insulators made of boron nitride. Inside the chamber, there is a spiral cathode filament made of the tungsten wire (diameter of 0.75 mm). The cathode is heated by the filament current (usually 25-35 A). The discharge burns in the area between the anode and cathode, the typical value of the anode (discharge) voltage is 30-40 V for the discharge current I_a up to 4 A. The ion source chamber is placed inside the electromagnet coil. The magnetic field of that coil partially compensates the field from the spiral cathode and plays an important role in placing the plasma near the extraction opening of the diameter ~0.8 mm.

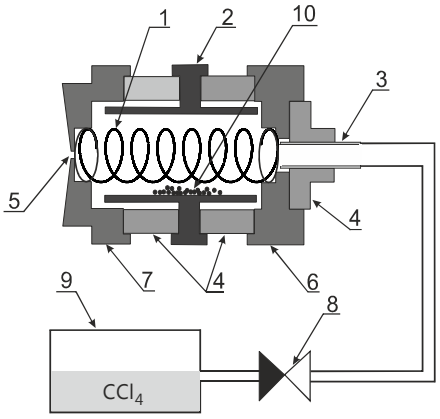

Fig.1. Schematic view of the ion source: 1 – cathode filament, 2 – anode, 3 – vapor inlet, 4 – insulators, 5 – extraction opening, 6–7 – cathode filament caps, 8 – dosing valve, 9 – CCl4 container, 10 – oxide powder

Small amount (~100 mg) of the rare earth oxide powder is placed onto the inner anode and cathode mount walls. Rare earth oxides are characterised by very high melting points (Eu_2O_3 – 2350°C, Gd_2O_3 – 2420°C, Ho_2O_3 – 2415°C, Pr_2O_3 – 2183°C) making it extremely poor feeding substance for ionisation. However, applying reactive component like CCl_4 improves usefulness of these oxides. CCl_4 vapours are transported into the chamber using a capillary through a dosing valve. The typical CCl_4 leak is 10-15 mbar cm^3/s.

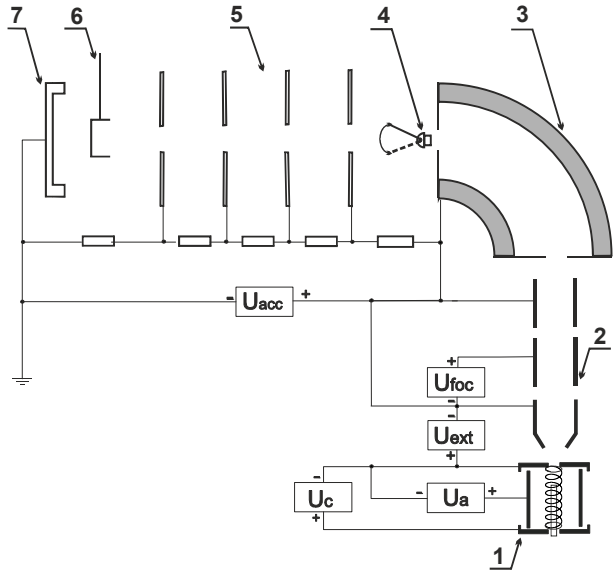

Fig.2. Scheme of the experimental set-up: 1 – ion source, 2 – extraction system, 3 – separating electromagnet, 4 – ion beam scanner, 5 – accelerator tube, 6 – Fraday cup, 7 – sample holder

There at least two paths the non-volatile rare earth's oxides could be converted into chlorides in the presence of CCl_4 in high temperatures. One of them is destructive adsorption of CCl_4 on the oxide surface, resulting from Cl and O atoms diffusion into the oxide bulk and gradual transformation of the oxide into chloride [22]. This reaction could be written as

(1) $3/2\ CCl_4 + RE_2O_3 \rightarrow 2RECl_3 + 3/2\ CO_2$,

where RE stands for any (III) rare earth.

CCl_4 may also undergo thermal decomposition, some possible reactions are listed below [23]:

(2) $Cl + CCl_4 \rightarrow CCl_3 + Cl_2$
(3) $2\ CCl_3 \rightarrow C_2Cl_5 + Cl \rightarrow C_2Cl_4 + 2Cl$
(4) $2\ CCl_2 \rightarrow C_2Cl_3 + Cl \rightarrow C_2Cl_2 + 2Cl$.

The next steps will be explained for the case of Eu_2O_3. Europium oxide could react with chlorine and form solid europium oxychloride EuOCl in the temperatures above 250°C [24]. EuOCl may undergo further chlorination in temperatures above 850 °C and form $EuCl_3$. The following production of europium (or any other rare earth) ion in the plasma chamber was already described in [16]. The chloride decomposes and atoms are ionised by electron impact in the discharge burning between the cathode and the anode. Ions are extracted via the extraction opening using the voltage V_{ext} = 25 kV. The extracted and formed beam enters a 90° sector separating electromagnet. The separated beam is additionally accelerated using V_{acc}=75 keV. The currents of mass-separated beamlets are measured using a Faraday cup placed behind the acceleration stage. The schematic view of the experimental set-up is shown in Figure 2.

Results

Characteristics of the ion source were measured ~20 min after ignition of the discharge, when it is stabilised. Measurements were done for Eu_2O_3, Gd_2O_3, Ho_2O_3 and Pr_2O_3.

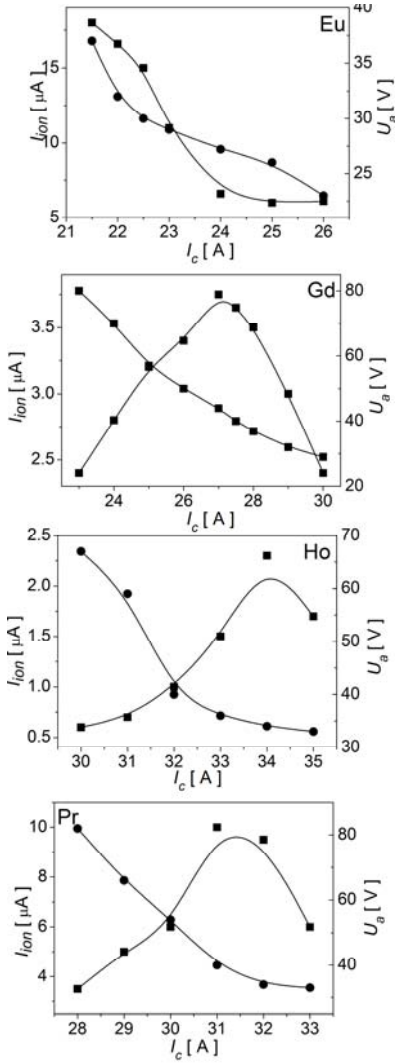

Fig.3. Dependences of the ion current and discharge voltage on filament current I_c

Figure 3 shows changes of ion current with Ic. Ion current initially grows with the cathode current – it is the effect of the increasing temperature as well as electron density. On the other hand, larger plasma density leads to the decrease of the discharge voltage. Consequently, the energy of electrons accelerated by this voltage also decreases, making the ionisation efficiency smaller. One deals with these two competitive trends that result in a Iion(Ic) curve having maximum for the optimal cathode current. The discharge voltages in the range 50-40 V seem to be optimal for all tested substances. It should be noted that such U_a for europium oxides is achieved for lower values of filament current (~21 A) and only the descending slope of the $I_{ion}(I_c)$ curve is presented in the figure.

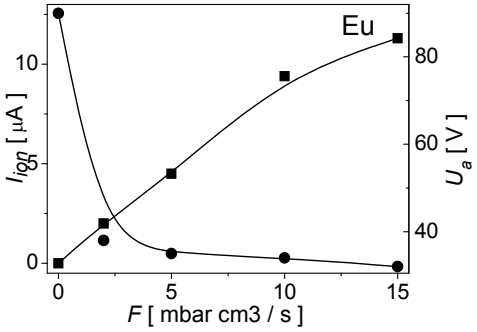

Fig.4. Changes of the ion current and U_a on CCl_4 leak.

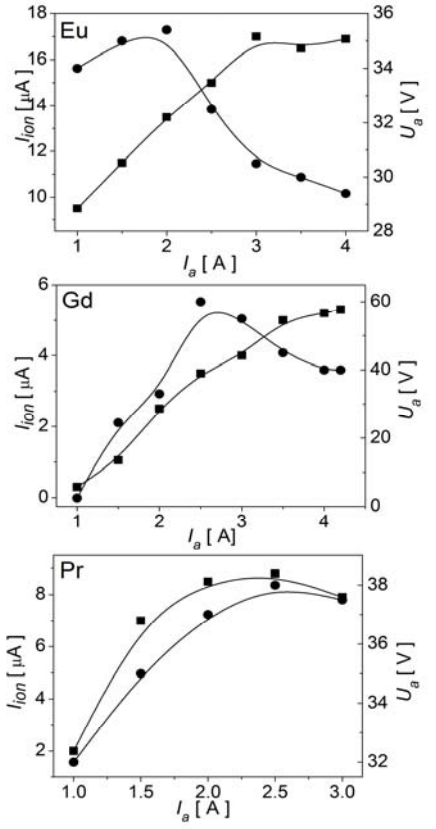

Fig.5. Dependences of the ion current and discharge voltage on discharge current I_a.

As one may expect the rare earth ion yield strongly depends on CCl_4 leak, as the reactive gas needed for the internal chemical synthesis of chlorides. Figure 4 shows dependences of Eu^+ current and discharge voltage as the function of carbon tetrachloride leak. The ion current rises almost linearly with F and Eu^+ is supressed after the dosing valve is shut off. However, one should have in mind that high CCl_4 leak leads to poorer vacuum conditions, which may lead to sparking between extraction electrode and ion source. A rapid increase of discharge voltage up to 90 V is observed, as CCl_4 plays a role of the carrier gas.

Figure 5. presents the dependences of the extracted current of Eu^+, Gd^+ and Pr^+ on the discharge current Ia . The other working parameters (including cathode current and magnetic field flux) are kept constant. Nearly linear dependence of these currents could be seen for lower I_a (< 2 A for Pr_2O_3 and < 3 A for Eu_2O_3 and Gd_2O_3) as the electron density and the ionisation probability increases. Saturation is observed for Eu_2O_3 and Pr_2O_3 as a consequence of anode voltage fall. The screening properties of plasma may have influence on the efficiency of ion extraction, making it less efficient when the plasma density increases. Also in this case the optimal discharge voltage near 40 V is optimal, resulting in the currents of 18 μA, 8 μA and 5 μA for Eu^+, Pr^+ and Gd^+, respectively.

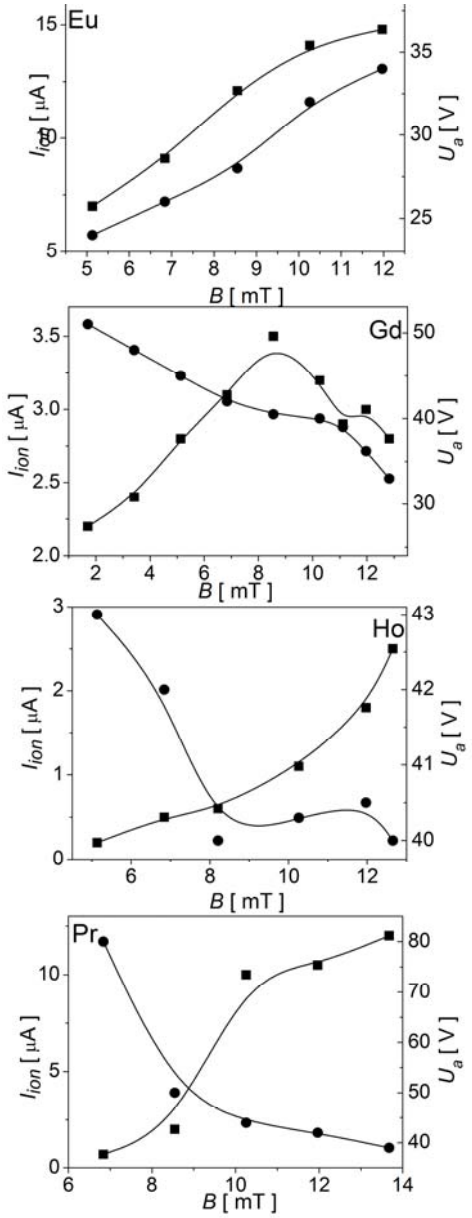

Fig.6. Dependences of the ion current and discharge voltage on magnetic field flux density B.

In order to check the influence of magnetic field on the ion current yield, the dependences of ion current and

discharge voltage on the magnetic flux density from the ion source electromagnet coil were determined. Measurement results are shown in Figure 6.

The magnetic flux density was measured using the LakeShore model 450 gaussmeter. For effective Eu^+, Ho^+ and Pr^+ production as high as possible (12-14 mT). In the case of Gd. a maximum for B = 9 mT was observed, which is slightly higher than a typical value for most of the solids used as a feeding substances. A typical $U_a(B)$ trend is observed for Gd, Ho and Pr oxides – anode voltage falls with the increasing plasma density and stabilises near its optimal value ~40 V.

Conclusions

In the paper the method of rare earth's ion production in the plasma ion source is described. Vapors of CCl_4 and rare earth's oxides are used as feeding substances – more volatile rare earth's chlorides are produced by internal synthesis in elevated temperature. The mechanism of such synthesis is proposed and described in the paper. The ion source was tested using Eu_2O_3 , Gd_2O_3, Ho_2O_3 and Pr_2O_3. Basic working characteristics of the ion source were measured, including the dependences of extracted ion currents on filament and discharge currents as well as on magnetic field flux density. The optimal value of the discharge voltage was ~40 V for all the tested substances. Rather high values of magnetic flux density are required (typically ~12 mT or even more) for effective ion production and extraction. The maximal ion currents of 18 μA, 5 μA, 3 μA and 12 μA were obtained for Eu^+, Gd^+, Ho^+ and Pr^+, respectively, which makes the described method useful for implantation purposes.

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