Arc discharge ion source for europium and other refractory metals implantation

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The best method for the impurity doping to the host material is the ion implantation. Due to high melting point of the rare earth standard metal ion sources are useless. One of the solution is to use chemical compounds of rare earths characterized by low melting point. In this paper we describe the novel design of the ion source suitable for refractory metal (e.g., rare earths) ion implantation. The dependencies of Eu^+ current on cathode and arc currents as well as on hydrogen flow are presented. Europium (III) chloride as the source of the europium atoms was used. Europium ions were produced during collisions of evaporated and decomposed $EuCl_3$ molecules with fast electrons. The typical current of the europium ion beam extracted from the ion source was 25 μA for the extraction voltage of 25 kV. The ion source works without maintenance breaks for approximately 50 h, which enables high dose implantation. The presented ion source needs neither advanced high power supplies nor high vacuum regime. © *2009 American Institute of Physics.*
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I. INTRODUCTION

The ion implantation is the most commonly used technique in the semiconductors industry to modify the optoelectronic properties of the solids. The most promising candidate for the new type light emitters based on the silicon technology are the SiO_2 and Si layers doped with rare earth (RE) due to their specific optical properties. Recently, it has been shown that Eu implanted SiO_2 layer can be used as the switchable two color light emitting device.[1] ZnO doped with RE shows the magnetic properties, which are very interesting in the field of spintronic.[2,3] In order to control the depth profile and fluence of doped elements the ion implantation is the best technique which can be used. The RE implantation augments many problem mainly due to their very high melting point. The RE ion generation process is very specific and the efficiency of the metal ion source depends on the many parameters such as ionization cross section, ionization potential, melting point, and the like. Therefore novel types of ion sources are designed and intensively investigated.

The efficiency of the metal ion source can be increased by lowering the melting point of substance introduced to the evaporator. One of the method is to use liquid alloys which consist of RE and another metals (Ni, Fe, Cr). In the case of Er–Ni alloy the melting point decreases from 1529 °C for Er down to 765 °C for the binary alloy.[4] Bischoff and Teichert[5] developed alloy consisted of $Er_{70}Fe_{22}Cr_5Ni_3$ characterized by melting point of about 860 °C. Such alloys are mainly used for the liquid metal ion sources. The ion currents of the Er atoms were in the range of hundreds nanoampere.[4] Hence, such alloys are used for the focus ion beam technique but not for semiconductor doping. Another kind of ion source is metal vapour vacuum arc (MEVVA) type ion source or ion sources with surface ionization, which is efficient but power consuming.[6,7] One of the most interesting designs is electron impact ionization ion source with electron beam heated anode reservoir.[8]

The aim of this work was to develop an efficient simply handling ion source for the purpose of RE elements ion implantation. As the source of the RE atoms we have chosen the chloride compounds of RE element due to their much lower melting point than RE metals. In this paper we present the europium ion source with evaporator heated directly by a cathode. As the source of europium, europium (III) chloride ($EuCl_3$) with melting point of 632 °C was used. The melting point of $EuCl_3$ is almost 200 °C lower than that for metallic europium. The typical ion beam current of europium obtained in the experiment was 25 μA for the 25 keV extraction voltage. The scheme of the ion source and main parameters are reported.

II. CONSTRUCTION AND DESIGN

Recently, great interests of RE ion implanted solids have been taken over the world due to their specific optical, electrical, and magnetic properties (Ref. 9 and references therein). Besides erbium, europium is one of the most important RE elements in the field of optoelectronic and magnetism. Due to high melting point of the RE metals the production of its ions is problematic.

In most cases of different types of ion source, ions are produced during collisions of atoms with fast electrons. Therefore, implanted elements have to be introduced to the collision range of the ion source chamber in the gas state. Typical gas pressure for the effective ionization yield is in the range of $10^{-2}-10^{-4}$ Torr. In order to produce metal ions the evaporator is needed. In the case of metals with high melting point (e.g., RE) it is difficult; due to the fact that

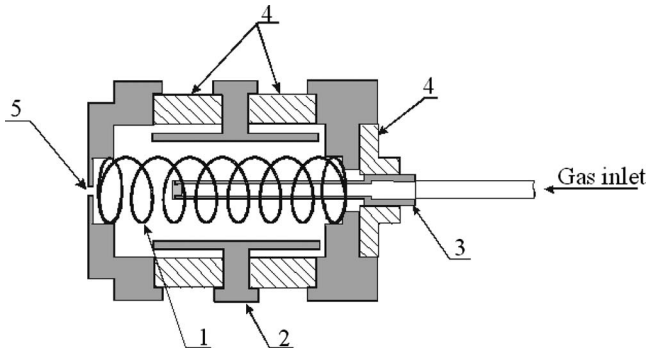

FIG. 1. Schema of the arc discharge ion source with evaporator. (1) a cathode, (2) an anode, (3) an evaporator, (4) isolators, and (5) an extraction opening.

high power is supplied, an additional cooling system is needed what significantly increases costs of the system and makes it more complicated.

We have designed an arc discharge ion source with evaporator for refractory metal ion implantation (see Fig. 1). Because the evaporator is heated by the surrounding spiral cathode, the power consumption of our ion source is reasonably reduced. The evaporator is heated both by electrons emitted from the cathode and arc discharge. In this way the maximum temperature obtained by the evaporator is approximately up to 2000 °C. Taking into account higher evaporation coefficient at low pressure it is possible to obtain ions of different metals with melting point above 2000 °C. The power consumption of our ion source with tungsten cathode in the operating mode is up to 350 W. The cathode is made of a 0.75 mm diameter tungsten wire. The typical current needed for cathode heating is about 28 A. In order to increase the electron emission from cathode and to reduce the supplied power, the cathode can be made of metals with lower work function e.g., tungsten reached by thorium. The spiral cathode is 20 mm long and has 6 mm in diameter. The typical lifetime of the cathode depends on the material of which the cathode is made and it approximates around 50 h for tungsten and 70 h for thorium reached tungsten. The evaporator, anode, and another metal parts of ion source chamber are made of molybdenum. Electrons emitted from the cathode are accelerated by voltage $U=U_A-U_K$, where U_A is the anode potential and U_K is the cathode potential on the minimum path of 1.5 mm. Boron nitride is used as the insulator. Internal volume of the ion source chamber is 1200 mm^3. The operating voltage applied to the anode U_A is in the range of few volts up to 100 V at arc discharge current up to 4 A. In order to increase electron impact ionization probability the ion source is embedded in the magnetic field. Evaporator is electrically insulated from the cathode and put in the cathode up to 3/4 of its length. The temperature of the evaporator could be controlled by the depth it is introduced into the cathode—different metals require different evaporator temperatures, depending on their melting point. We have chosen RE (III) chloride as the source of the RE ions. Europium (III) chloride characterizes about 200 °C lower melting point than metallic europium (826 °C) and decomposes on Eu and Cl at 632 °C. Moreover, the metallic europium could be easily oxidized in air. The Eu_2Cl_3 is highly hygroscopic—after contact with air anhydrous Eu_2Cl_3 rapidly absorbs water creating hexahydrate $Eu_2Cl_3\times 6H_2O$. The construction of the ion source enables a gas flow during its heating and operation.

The distance between the wall of evaporator and cathode is 1 mm. The outlet of the evaporator is closed with a flow reductor. Ions generated in the discharge arc are extracted from the volume of the ion source through 1 mm diameter extraction opening. The extraction voltage can be changed from a few hundreds volts up to 30 kV. The mass analyzes of the ions emitted from the ion source were carried out by means of the magnetic field with mass resolution $\Delta R=400$.

III. RESULTS AND DISCUSSION

A. Numerical simulations

In order to check the influence of parameters such as electron density in the arc, temperature, extraction voltage on the ionization efficiency, and ion yields, a numerical model of the source has been developed. The code follows trajectories of particles trapped inside the ionization chamber. The potential distribution is determined by boundary conditions—it corresponds to anode voltage $U_a=40$ V. The potential in the discharge area is assumed to be nearly flat, with potential value near the ionization potential of europium. The anode fall is also reproduced by appropriate boundary conditions. Particles are extracted through the extraction opening of 1 mm diameter. The distance from the hole and the flat extraction electrode is 1 cm. The value of extraction voltage was changed up to 25 kV. Simulation area has been covered with three-dimensional spatial grid. The dimensions of the grid cells are $\Delta x=\Delta y=\Delta z=0.1$ mm. The potential distribution is found by solving Poisson equation using successive over-relaxation method.[10] Equations of motion are integrated via fourth order Runge–Kutta method. Neutral Eu atoms are emitted from the evaporator. Their initial velocities correspond to the evaporator temperature $kT_i=0.15$ eV. Neutral atoms could be ionized by collisions with fast electrons. The mean path the atom travels inside the arc plasma until it is ionized could be estimated by a formula

$$\lambda(T_e,n_e)=\left[n_e\int_0^\infty \sigma(E)f(E,T_e)dE\right]^{-1}, \quad (1)$$

where $\sigma(E)$ is electron impact ionization cross section for europium,[11,12] $f(E,T_e)$ is Maxwell–Boltzmann distribution corresponding to the arc electron temperature T_e, and n_e is the concentration of electrons. The Monte Carlo method based subroutine calculates probability of the atom ionization depending on the passed path,

$$\lambda_i=-\lambda(T_e,n_e)\ln(RND), \quad (2)$$

where RND is a pseudorandom number from the range (0,1).

The code counts the number of ions N_+, as well as neutral atoms N_o, passing the extraction opening. The ionization efficiency of the source is defined as the ratio of the number of extracted ions and the number of all particles leaving the source,

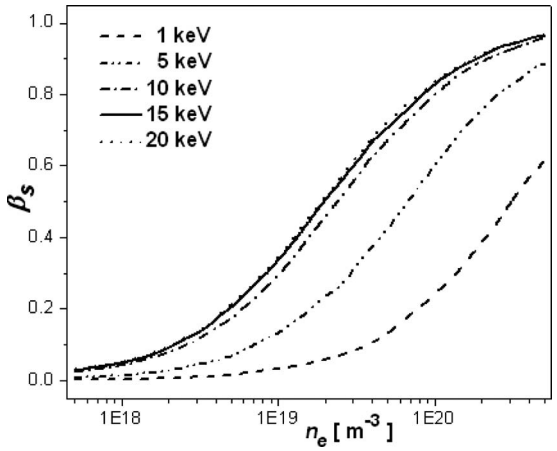

FIG. 2. Ionization efficiency β_s for different values of extraction voltage.

$$\beta_s = \frac{N_+}{N_o + N_+}. \tag{3}$$

Calculations of the ionization efficiency for different values of extraction voltage have been performed. Figure 2 shows the ionization efficiency as the function of electron concentration.

As one can see the ionization efficiency increases with n_e–according to formula (1), the larger electron density the shorter the path atoms travel until they are ionized by electron impact. For $n_e = 10^{19}$ m^{-3} and typical extraction voltages the efficiency reaches 40%. Large electron concentration is one of the crucial factors resulting in high source efficiency. Hence, large anode currents are desirable. The source efficiency increases fast with the extraction voltage. This is due to the fact that the electric field enters the source volume deeper, and ions are extracted fast from the ionization chamber. Figure 3 presents a typical current-voltage curve obtained from simulations.

Initially, the ion current increases fast with U_{ext}—it fits well the Child–Langmuir law.[13] On the other hand, for larger U_{ext} the rate ions are extracted from the source reaches the rate they are produced. A saturation of current-voltage curve is observed.

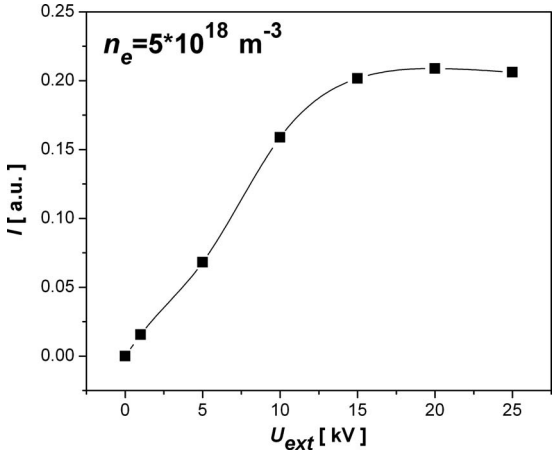

FIG. 3. Current-voltage curve predicted by numerical simulations.

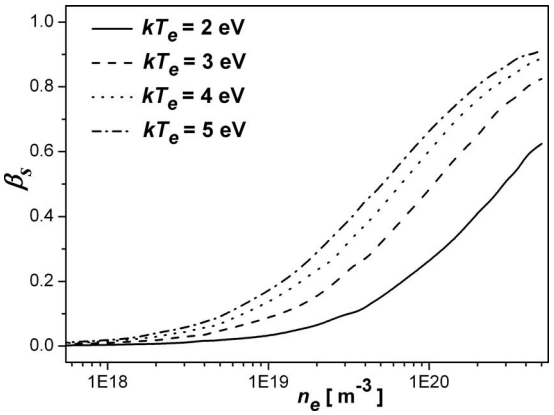

FIG. 4. Influence of electron temperature on ionization efficiency.

One may expect that the source efficiency grows with electron energy—the electron impact ionization cross section increases fast with energy and in the case of europium reaches its maximum for 10 eV. This is confirmed by simulation results, the ionization efficiency is strongly affected by electron temperature (Fig. 4). Calculations have been made for typical electron temperatures of the arc (2–5 eV).

In the case of $n_e = 10^{19}$ m^{-3} the increase in the electron temperature from 2 eV up to 4 eV increases the source efficiency more than fourfold (from approximately 3% up to 13%). Thus, the high energy of electrons (due to high anode voltage and cathode temperature) results in effective ionization and large ion currents.

B. Experimental

The heating of the evaporator was performed in hydrogen atmosphere in order to avoid EuOCl formation. The Eu^+ ion beam produced by the arc discharge ion source is extracted by extraction electrode on potential of 25 kV. The yield of the ion source was measured as the function of the cathode current, arc discharge current, magnetic field, and rate of the hydrogen flow.

Figure 5 shows the change in the Eu^+ current beam and anode voltage as functions of the cathode current. During this test the arc current, magnetic field, and rate of the hydrogen flow were kept constant. An increase in the cathode

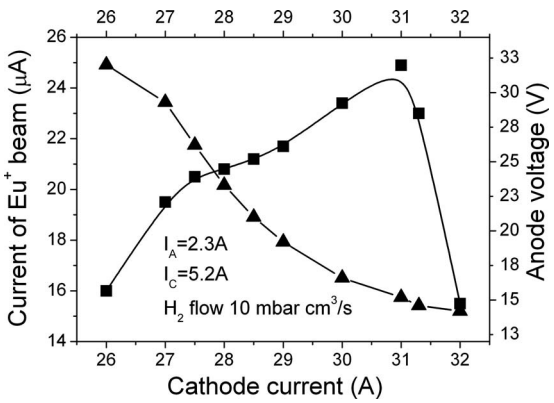

FIG. 5. Change in the Eu ion beam current (square symbol) and anode voltage (triangular symbols) as functions of the cathode current. The arc current, magnetic field, and hydrogen flow were constant.

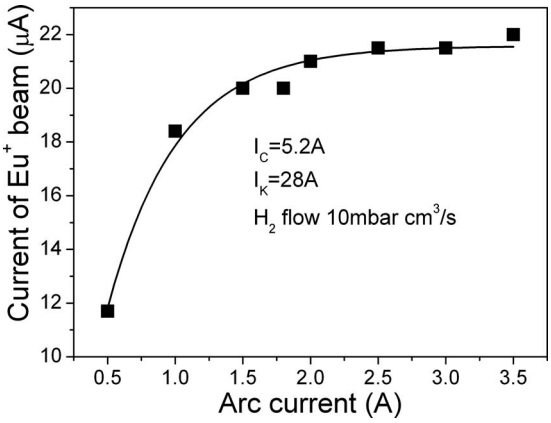

FIG. 6. Change in the Eu ion beam current as a function of the arc current under constant hydrogen flow (10 mbar cm^3 s^{-1}), current of magnetic field (5.2 A) and cathode current (28 A).

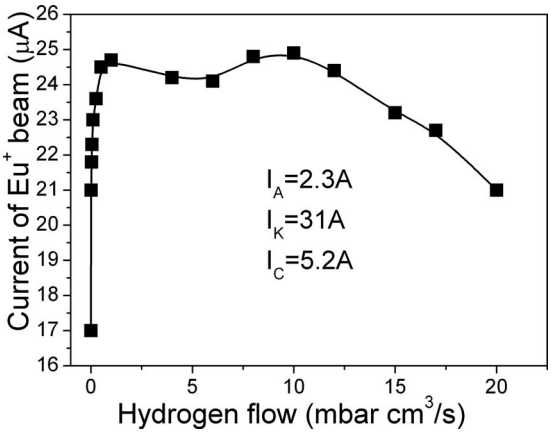

FIG. 7. Influence of the H_2 rate flow on the europium ion beam current. The cathode current, solenoid current, and arc discharge current were 31, 5.2, and 2.3 A, respectively.

current increases both the temperature within the ion source and density of the electrons emitted from the cathode, what decreases the anode voltage (for constant arc discharge current). Europium ions are produced by collisions of the evaporated Eu atoms with fast electron in the ion source chamber.

The ionization potential of Eu is 5.61 eV.[14] For the efficient ionization process of the europium atoms the energy of electrons must be at least twice as large and high density of electrons is needed. One deals with two concurrent tendencies predicted by simulations: ionization efficiency increases with electron density and cathode temperature, on the other hand increasing electron density reduces the anode voltage, which degrades the ion current. Therefore, in order to obtain an efficient ionization it is necessary to find the compromise between most important parameters of the arc discharge ion source (cathode current, density and energy of electrons, and evaporator temperature). As can be seen in Fig. 5 an increase in the cathode current from 26 up to 31 A increases the current of the europium ion beam. However, further increase in the cathode current decreases the ionization yield. For this investigation anode power supply with current stabilization was used. Therefore, at constant arc discharge current the anode voltage depends on the electron density. An increase in the electron density decreases the anode voltage, which leads to decrease in the electron energy and ionization yield. The highest Eu^+ beam current was obtained for 31 A of the cathode current.

We have investigated an influence of the arc discharge current change on the ionization efficiency of the europium atoms as well (see Fig. 6). At constant cathode current an increase in the total europium ion beam current with increase in the arc current to the certain level was observed. This is in a good agreement with simulation results: ionization yield increases rapidly with electron density and electron arc temperature. Moreover, the evaporator is manly heated by arc discharge. An increase in the arc current increases the temperature of the evaporator. Therefore, higher amount of the europium atoms is introduced into the ionization area. On the other hand, for arc currents above 2.5 A one can observe saturation of extracted ion current. This could be explained by increasing (with n_e) probability of Eu^+ ion recombination. Additionally, higher plasma density makes the extraction process less efficient, due to better screening properties.

As was mention above, the key role in our europium ion source plays hydrogen. Therefore, an efficiency of the ionization process of the europium atoms as a function of the hydrogen flow was investigated. Figure 7 shows the change in the Eu^+ beam current as a function of the hydrogen flow. The rate of the hydrogen flow was decreased during measurements in order to avoid EuOCl formation. It should be noticed that the measurement without hydrogen flow was done 5 min after closing the flow valve. Without the flow the ion current decreases, as the source is running out of residual hydrogen. The highest europium beam current for the H_2 flow at 10 mbar cm^3 s^{-1} was obtained. At the maximum ion current the operation time of the ion source without interruption depends on the amount of $EuCl_3$ introduced to the evaporator. Using the load of 4 mg of the $EuCl_3$ 25 cm^2 area may be implanted with the dose of 10^{17} ion/cm^2. The stability of the ion current during operating mode was below 1%.

The described in the paper arc discharge ion source was tested for different metals (Er, Tb, Sm, Al, In, Cu, and Fe) as well. For RE (Er, Tb, Sm) the ion beam current was around 2 μA. The 100 μA ion beam current for the Cu and Fe was obtained. In case of the Al and In the ion beam current was 120 and 250 μA, respectively. During the measurements the Mo ion beam current in the level of 20 μA was observed as well. The Mo ions are emitted from the evaporator by plasma sputtering.

IV. CONCLUSIONS

We have designed an arc discharge ion source with evaporator for the ion implantation of the refractory metals. Due to its lower melting point (compared to RE metals) we have used chlorine compounds. Numerical simulations suggest that high temperature of the arc as well as large concentration of electrons results in high ion yield. This is confirmed by experimental measurements of ion current as functions of cathode and arc currents. In the case of REs, the highest ion beam current was obtained for europium. The ion

source yields 25 μA of Eu^+ with ion current stability below 1%. Using the load of 4 mg of the $EuCl_3$ 25 cm^2 area may be implanted with the dose of 10^{17} ion/cm^2. The RE ion currents provided by the described ion source are comparable (or better) to those given by sources of other design.[4–8] The advantage of our source is compact construction, low power consumption, and a simple maintenance.

ACKNOWLEDGMENTS

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