# Pulsed source of metal atoms and their compounds

D. A. Chestakov, A. Zawadzka, and D. H. Parker
*University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

K. V. Vidma and A. V. Baklanov
*Institute of Chemical Kinetics and Combustion, Institutskaja St. 3, Novosibirsk 630090, Novosibirsk State University, Pirogova St. 2, Novosibirsk 630090, Russia*

S. A. Kochubei
*Institute of Semiconductor Physics, ac. Lavrent'yev Ave., 13, Novosibirsk 630090, Russia*

A pulsed source for production of metal atoms and their oxide compounds in a supersonic expansion is described. The design utilizes a simple pulsed valve and produces a concentration of $10^6 - 10^7$ atoms per $cm^{-3}$ of the desired metal atoms in a molecular beam. Depending on the carrier gas used, metal compounds at similar concentration levels can also be produced. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1841952]

With the growth of nanoscale technologies new interest has developed in the properties of metals and their compounds. Modern device designs, as in Refs. 1 and 2, require a detailed insight in material properties. However, the electronic structure of many metal atoms and their compounds is not yet well understood. In general, the major problem of spectroscopic studies in this area is to bring the single atom (or molecule) into the gas phase. Two commonly used techniques are laser ablation and thermal vaporization. Laser ablation requires a dedicated laser and the second method needs a high temperature oven. Both methods can result in a broad temperature distribution of sample particles and/or extensive clustering.

Studies of metal atoms and their compound properties can be made easier by using a convenient atom source. We describe here a pulsed source of metal atoms and their compounds based on the cathode sputtering effect, which has several advantages:

(1) It is a simple metal wire;
(2) It is an efficient and clean source for spectroscopic and imaging studies;
(3) It requires no heating and no laser for operation;
(4) Free metal atoms are produced in the expansion region of a molecular beam, leading to cooling;
(5) The choice of carrier gas can also allow production of a desired metal compound.

It is well known that hollow cathode glow discharges are efficient sources of metal atom vapor and metastable species.[3] Grove discovered cathode sputtering in 1852.[4] The effect was carefully studied and a number of papers have been published on the mechanism of sputtering for all kinds of electrodes: metals, alloys, semiconductors, dielectrics in solid and liquid phases, various crystal, and amorphous structures. The composition of sputtered samples, their angular and energetic dependence on the discharge parameters, electrode shape, etc. was also examined and information was collected and csystematized.[5–13] Such a strong interest in this subject is explained by its applications: surface cleaning,

which was first applied by Strong;[14] thin film deposition; ion etching;[4,15–17] chemical reactions of sputtered products with carrier gas;[18] and mass-spectroscopy applications.[19]

Thermal vaporization has been used for a long time to bring high melting point materials into the gas phase. Alternatively, starting from early 1980s, laser vaporization of the target species[20–22] became extremely useful for introduction of samples into supersonic beams. In this paper we suggest combining supersonic beams with cathode sputtering. This method is much more simple and cheaper than the above-mentioned methods.

In our experiments[23] we have recently found that metal atoms can be introduced into a molecular beam by the use of a simple design, which is schematically shown in Fig. 1. In this figure ceramic holder installed on the top of a standard pulsed molecular beam nozzle (General valve, pulse duration $\sim 300$ $\mu$s) holds a discharge wire of $\varnothing 0.5 - 1$ mm, which is made from the desired material and curled into a ring shape of $3 - 4$ mm in diameter and held $\sim 3$ mm above the nozzle exit. A high voltage dc supply (Brandenburg, HV current limit $\sim 1$ mA) delivers $-2000$ V to the discharge wire (cathode). The stainless steel body of the nozzle is grounded and operates as the second electrode (anode). When the nozzle is opened, a discharge is initiated in the molecular beam and the cathode atoms are sputtered from the electrode. Some of these atoms are taken up or react with the gas from the nozzle, the rest deposit on the surrounding surfaces. For some materials like silicon a simple plate electrode with a hole in it also works well, as in Fig. 1(b), where a photograph of the source with silicon electrode is shown.

The source was tested in a velocity imaging setup and in a time-of-flight setup by observing different products and estimating their concentrations. In order to explain this procedure, we must first review the principle of velocity map imaging, shown in Fig. 2. The nozzle produces a molecular beam pulse, which passes through a skimmer into the ion lens system. Ions created by the laser pulse passing between the repeller (R) and extractor (E) are accelerated through the ground electrode (G) opening towards the 2D multi-channel
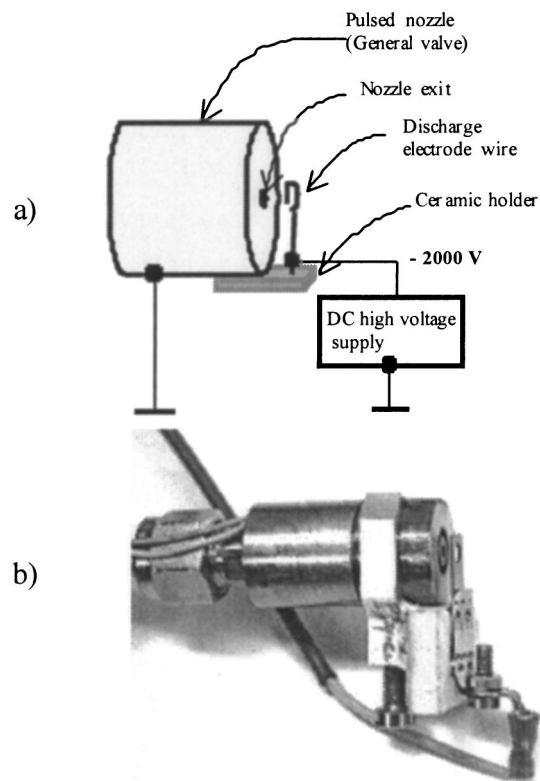
FIG. 1. (a) Setup producing the pulsed source of metal atoms and their compounds. (b) Photograph of the source using a General Valve, for the production of silicon atoms.

plate detector (MCP). Gating the MCP detector at the proper arrival time selects a particular mass. Voltages on the ion lens electrodes are set in such way that ions having the same mass and the same $v_x$ and $v_y$ velocity component fall on the same spot of the MCP detector, independent of where they were formed. The MCP detector converts ion signal into electrons, which create light flashes on the phosphor screen. A charge coupled digital (CCD) camera records the resulting image, which is stored on the computer (PC). The images are 2D projections of the 3D velocity distribution of photolysis products. With the help of special software one can restore the initial 3D velocity distribution. The system counts single ions, measures kinetic energies of the photofragments, and their angular distributions with respect to the photolysis laser polarization.
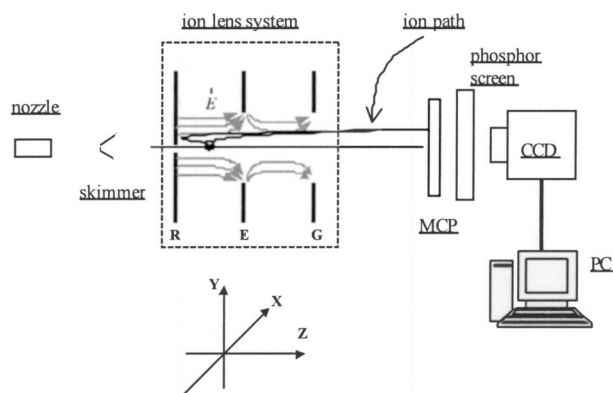


FIG. 2. Schematic diagram of a velocity map imaging apparatus.
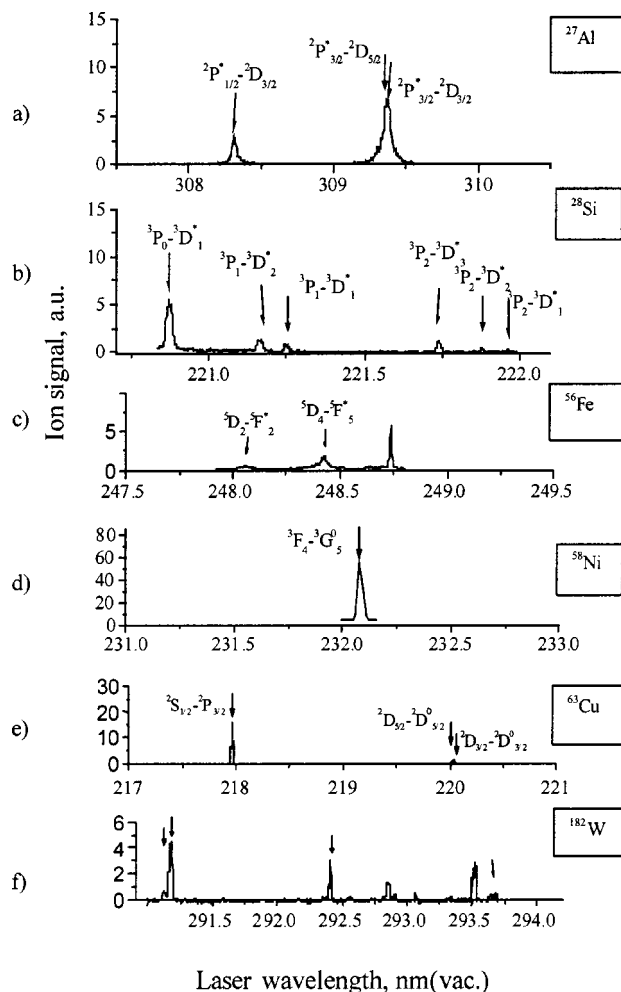


Laser wavelength, nm(vac.)

FIG. 3. Ionization yield spectrum of atoms (labeled on the left side of the figure), recorded with a discharge in argon with different cathodes. The ion masses have also been measured by time-of-flight and their values are shown in rectangular insets on the right side of the plots. The following cathode materials were used: (a) aluminum; (b) silicon; (c) iron; (d) nickel; (e) copper; (f) tungsten. The arrows mark known and assigned emission lines of each element. Note that for tungsten there are no assigned states known in the region scanned.

The test of the atomic source included mass calibration, the identification of species by mass and resonance enhanced multiphoton ionization (REMPI) spectrum and estimations of the particle concentration in the molecular beam. During our experiments the following materials have been used as electrodes: iron, aluminum, copper, nickel, tungsten, and sili-

TABLE I. Atom concentrations using the discharge in Ar and $O_2$ carrier gas with different electrodes. For atoms marked by (∗), the measurements have been carried out in the setup in Novosibirsk.

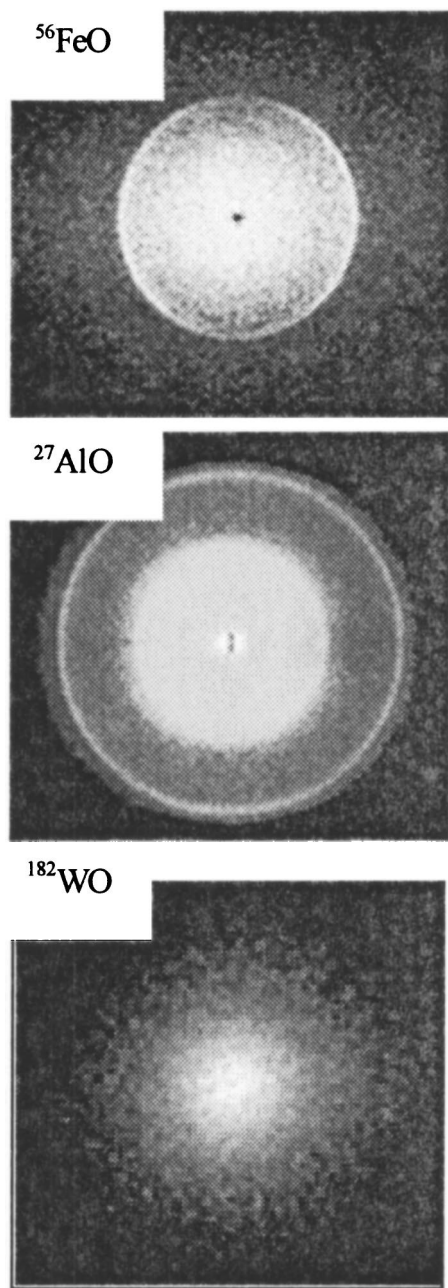| Atom | Concentration (in argon), $cm^{-3}$ | Concentration (in oxygen), $cm^{-3}$ | Concentration of oxide (in oxygen), $cm^{-3}$ |
|---|---|---|---|
| Silicon | $>10^6$ | ⋯ | ⋯ |
| Iron | $10^7$ | $2 \cdot 10^6$ [a] | $8 \cdot 10^6$ [a] |
| Copper* | $10^7$ | ⋯ | ⋯ |
| Nickel* | $2 \cdot 10^6$ | ⋯ | ⋯ |

[a]Reference 24.

FIG. 4. Raw images of metal atoms arising from the photodissociation of $^{56}$FeO, $^{27}$AlO, and $^{182}$WO molecules.



FIG. 5. The ionization scheme for Cu atoms.

con. The ionization spectra of particles found in each molecular beam are shown in Figs. 3(a)–3(e).

In most cases we have estimated the concentrations of the metal atoms in molecular beam after the skimmer. These values are listed in Table I and the estimation procedure is described in the Appendix.

Metal compounds can be produced by the use of the proper carrier gas. The dissociation of metal monoxides has been observed here when oxygen was used. Figure 4 presents a few examples of dissociation images of various metal monoxides.

The parent molecules (labeled in insets) dissociate into metal and oxygen atoms after absorbing a laser photon. The excess photon energy converts into kinetic energy of the atoms; t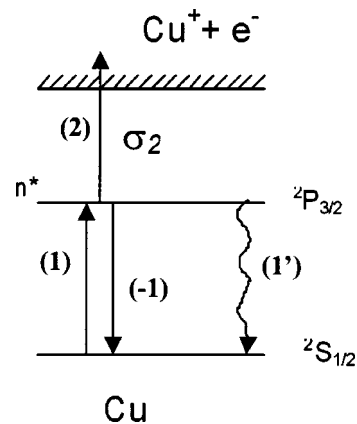hese fly apart and form the (Newton) spheres. The sphere of metal atoms is made "visible" by the apparatus after ionization of the atoms by $(1+1)$ REMPI at the appropriate wavelength. The velocity of the products (calculated from the size of sphere) and their angular distribution give the information about the bond energy and the nature of the electronic transition involved in photodissociation process. Table I shows the estimated values for concentrations of atoms and their oxides, obtained in the test.

In conclusion, in this note we have demonstrated the generation of molecular beams of metal atoms and their oxide compounds in a very simple apparatus. This generation can be improved to higher concentrations by using a larger cathode area and adjusting the discharge geometry.

## APPENDIX: ESTIMATION OF THE METAL ATOM CONCENTRATION IN THE MOLECULAR BEAM

The procedure for estimating of the atom concentration described for the example of copper. The $(1+1)$ REMPI scheme of atomic copper is shown in Fig. 5.

The power dependence of the yield of $Cu^+$ ions has been studied with unfocused laser radiation. The UV-pulse energy flux $F$ was varied within the interval $30-150$ $\mu J/cm^2$. The yield of $Cu^+$ ions was found to rise linearly with pulse energy. This allowed us to conclude that the laser driven processes $(\mathbf{1})$ and $(-\mathbf{1})$ dominate over the fluorescence $(\mathbf{1}')$ and balance the steady-state populations of the states $^2P_{3/2}$ and $^2S_{1/2}$ in compliance with their degeneracy factors. The steady-state concentration $(n^*)$ of excited $Cu(^2P_{3/2})$ atoms is thus of $2/3$ of the total current concentration $(n)$ of Cu atoms in their $^2P_{3/2}$ and $^2S_{1/2}$ states. Typical values of the cross section $\sigma_2$ of one-quantum ionization of excited atoms are of about $10^{-17}-10^{-18}$ $cm^2$,[25] and we choose the value $\sigma_2 = 3 \cdot 10^{-18}$ $cm^2$ for estimations. The yield $(Y)$ of $Cu^+$ ions can be evaluated as $Y \approx \frac{2}{3} \cdot \sigma_2 (F/h\nu) \cdot n$. The integral of the signal of $Cu^+$ ions (sum of both $^{64}$Cu and $^{65}$Cu isotopes) was used to determine the $Y$ number and then estimate the concentration $n$. Taking into account that only a minor part

($<5\cdot10^{-4}$) of the atoms are ionized by the laser pulse, the extracted $n$ value provides a good estimate for the initial concentration of the ground state $Cu(^2S_{1/2})$ atoms in the probing region of the molecular beam. These measurements have been carried out with voltages on the discharge circuit of $1-5$ kV and the carrier gas Ar with a backing pressure of $1-4$ bar. The maximum concentration value $n$ $\approx 10^7$ Cu atoms per $cm^3$ has been obtained with $U=5$ kV and $P_{back}=4$ bar. The signal of $Cu^+$ ions has also been detected with the laser wavelength tuned away from the resonant band [Fig. 3(e)]. This nonresonant signal appears in one-quantum ionization of long-lived metastable Cu atoms with energy within one photon ($h\nu=5.69$ eV) (Ref. 26) from the I.P.$=7.72638$ eV. The concentration of these metastables in the probe region was estimated to be about $10^2$ times less than the ground state concentration $n$.

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