Trace Element Analysis of Potassium by Resonance Ionization Mass Spectrometry

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A simple resonance ionization mass spectrometer is built with a quadrupole mass spectrometer (QMS) and two laser diodes aiming at trace analysis of potassium. The overall detection efficiency is estimated comparing the yields of resonance ionization and electron-impact ionization in the same QMS. A clear discrimination of $^{39}$K, $^{40}$K, and $^{41}$K is demonstrated with a help of isotope shifts of the atomic levels.

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1. Introduction

Recently, the evaluation technology of the trace substances has become important in many areas such as environmental science, biochemistry and semiconductor industry. As one of the effective methods for the trace element analysis, resonance ionization mass spectrometry (RIMS) is currently studied mainly with calcium (Ca) or strontium (Sr) atoms for isotope analysis.1,2) RIMS consists of two parts which are

2. Experimental Procedure

2.1 RIMS scheme

As mentioned above, RIMS method is the combination of the resonance ionization by lasers and the mass analysis.

Figure 1 shows the resonance ionization scheme of potassium employed in the present study. Two laser diodes were used for the single-resonance ionization of potassium gas atoms.

The first laser is a wavelength-tunable external cavity diode laser (ECDL; Sacher Lasertechnik SYS-100-405-20) operating in the wavelength range of $\lambda = 402.7 - 405.2$ nm. A single-mode 3.5 $\mu$m core diameter fiber is coupled to this laser system with an FC/APC connector. The wavelength was fine-tuned to $\lambda = 404.8356$ nm for the $4^2S_{1/2} \rightarrow 5^2P_{1/2}$ resonance excitation in vacuum ($\lambda = 404.7213$ nm in air),3 via the piezo actuator attached on the diffraction grating in the laser head. The piezo voltage can be controlled manually from the control panel knob in the range of 0–100 V, with a frequency sensitivity of $\Delta v = 2$ GHz/V (0.0011 nm/V). Higher piezo voltage means lower laser wavelength, or higher laser frequency. The maximum laser output was more than 40 mW, corresponding to the single-mode fiber output of more than 20 mW. This laser has not been frequency-locked yet in this work, so the wavelength drift occurred in the time span of a few minutes or longer.

The second laser is an Amonics model ALD-808-3000-B-FC laser diode for photoionization with a fixed wavelength of $\lambda = 808 \pm 5$ nm. A multi-mode 100 $\mu$m core diameter fiber is coupled to this laser system with an FC/PC connector. The maximum output was more than 3 W, corresponding to the multi-mode fiber output of more than 2.5 W.

We used a QMS (Pfeiffer Vacuum QMS200) for the mass analysis of potassium ions produced by the resonance ionization. It is equipped with a channeltron to detect ions as an amplified ion current.

2.2 Sample preparation

In this work, potassium gas atoms were obtained from the decomposition of $\text{K}_2\text{CO}_3$ in the electrothermally-heated graphite crucible. In each trial, 15 $\mu$L of 50% water solution of $\text{K}_2\text{CO}_3$ was loaded into the crucible. After drying the sample, the crucible containing the net weight of 14 ± 1 mg $\text{K}_2\text{CO}_3$, corresponding to 1.2 $\times$ 10$^{20}$ potassium (K) atoms, was set in the heating device (Epiphest THKC-200-SB).

As the crucible temperature increases electrothermally, the decomposition is assumed to occur as follows:4)

$$\text{K}_2\text{CO}_3(c) = \text{K}_2\text{O}(c) + \text{CO}_2(g).$$  (1)

The potassium atoms are obtained from the decomposition of $\text{K}_2\text{O}$ under the higher crucible temperature.
The observed two peaks are consistent with the hyperfine splitting (HFS) of $^{39}$K. See §3.3.2 for the detailed explanation.
Fig. 3. An example of the resonance ionization signal of $^{39}$K by scanning the piezo voltage $V_{\text{piezo}}$. The QMS ion current is shown as a function of time for the voltage scanning. The observed two peaks correspond to the hyperfine splitting (HFS) of $^{39}$K $^2S_{1/2}$ ground state. This figure represents the same data as $^{39}$K data of Fig. 8.

3.2 Overall detection efficiency

The overall detection efficiency is defined as the ratio of the number $N_D$ of potassium atoms detected by the QMS to that initially loaded in the crucible. $N_D$ could be experimentally determined by the time integration of the channeltron current until the $K_2CO_3$ sample in the crucible is evaporated away. Since we have not yet used the frequency-locking system for the laser of the resonance excitation, it is difficult to keep for a long time the laser frequency on-resonance with the transition to the excited state shown previously in Fig. 1. On the other hand, it is rather easy to estimate the overall detection efficiency $E_{EI}$ of EI ionization experimentally by integrating the channeltron current of EI ionized potassium. Therefore, RIMS overall detection efficiency $E_{RIMS}$ in this work can be determined by the short time measurement of the ratio $R$ of the detection efficiency by RIMS to EI: $E_{RIMS} = R \times E_{EI}$.

To estimate the detection efficiency $E_{EI}$, the sum of the channeltron current $I_{\text{mean}}$ of $^{39}$K$^+$ and $^{41}$K$^+$ has been measured from the beginning of the crucible heating ($t = 92$ s) until the $K_2CO_3$ sample was lost ($t = 25900$ s), which is shown in Fig. 4(a). It took about an hour to increase the crucible heating current from 0 A ($t = 92$ s) to 7.50 A, corresponding to the crucible inner temperature of $T \sim 300$ to 1170 K. After reaching the target temperature, the heating current was maintained at 7.50 A until the end of the measurement. Background channeltron current $I_{BG}$ has been estimated as the average of the channeltron current without crucible heating ($t = 0$–92 s). Integration of the net channeltron current $I_{\text{EI}} \equiv I_{\text{mean}} - I_{BG}$ over the time span of 92–25900 s yielded $5 \times 10^{-3}$ C, corresponding to $9 \times 10^{10}$ potassium atoms, which was $E_{EI} \approx 8 \times 10^{-10}$ of the initially loaded ones.

Figure 4(b) shows an experimental result of the channeltron current of $^{39}$K$^+$ atomic ions by RIMS and EI. The channeltron voltage in this figure was lower than that used in the measurement of Fig. 4(a). Therefore, the ion currents of Figs. 4(a) and 4(b) cannot be directly compared.

The crucible heating current was set to 7.50 A in advance. Throughout the measurement, the emission current of the thermal electron for EI ionization has been kept to 0.1 mA, in other words, the channeltron current contributed by EI ionization remained constant. In addition, two lasers were irradiated in four ways: (I) both were ON; (II) both were OFF; (III) 405 nm laser was ON and 808 OFF; (IV) 405 OFF and 808 nm laser was ON. Little difference was observed between the current of (II) and (IV), meaning that resonance ionization occurs only under the existence of the wavelength fine-tuned laser for resonance excitation. The ratio $R$ of the detection efficiency by RIMS to EI can be obtained as the ratio of the measured channeltron current of (I) subtracted by (II) to (II), which was $R \approx 8.3 \times 10^{-7}$ A/9.7 $\times 10^{-9}$ A $\sim 90$. Combined with $E_{EI}$ obtained above, RIMS overall detection efficiency $E_{RIMS}$ has been estimated to be $E_{RIMS} = R \times E_{EI} \sim 7 \times 10^{-8}$.

The improvement ratio of RIMS detection efficiency with the 808 nm laser over without it is estimated to be about a factor of 80 by comparing the net ion current of (I) to (III) with the effect of EI ionization (II) subtracted. This means that the resonance ionization occurs only with the 405 nm laser, but the ionization is highly effective with the 808 nm laser.

Fig. 4. Measurement of the channeltron current by RIMS and EI ionization for the estimation of the detection efficiency by each method: (a) measurement of the channeltron current by EI for the estimation of the detection efficiency and (b) comparison of the measured channeltron current between RIMS and EI. The channeltron voltage was set lower than (a). See text for details.
The resonance ionization probability of potassium atoms can be estimated by solving the rate equations. Though I showed the RIS scheme in Fig. 1, some additional excited states have to be taken into account in the rate equations to handle the spontaneous emission from the $5p_{1/2}$ to these states and the successive spontaneous emission from them. Detailed RIS scheme of potassium is then shown in Fig. 5. Numbers 1–6 correspond to the states in Table I, respectively. The parity is indicated by appended degree symbols on odd parity terms in this table.

In the case of $4S_{1/2} \rightarrow 5P_{1/2}$ transition, the cross section of stimulated emission from the $5p_{1/2}$ excited state is the same as that of resonance absorption, $\sigma_{a} = \sigma_{s}$, because of the equal statistical weights of the $4S_{1/2}$ ground and the $5p_{1/2}$ excited states (see Table I). Table II shows numerical values of each spontaneous emission rate $A_{st}$. The population of each state under stationary conditions can be estimated by solving the rate equations.

The population of each state under stationary conditions is given by the following rate equations:

$$
\begin{align*}
\dot{n}_1 &= -Rn_1 + (R + \Gamma)n_2 + A_{S1}n_S + A_{S1}n_0 \\
\dot{n}_2 &= Rn_1 - (R + \Gamma + I + A_{S2} + A_{S2})n_2 \\
\dot{n}_3 &= A_{S2}n_2 - (A_{35} + A_{S3})n_3 \\
\dot{n}_4 &= A_{S3}n_3 - (A_{45} + A_{S4} + A_{S4})n_4 \\
\dot{n}_5 &= A_{S4}n_4 - (A_{S5} + A_{S6} + A_{S6})n_5 \\
\dot{n}_6 &= A_{S6}n_5 - A_{S6}n_6 \\
\dot{n}_7 &= I_n 
\end{align*}
$$

where $\dot{n}_i = dn_i/dt$ ($k = 1, 2, \ldots, i$), $R = \sigma_{a}F_{a} = \sigma_{s}F_{s}$ and $I = \sigma_{I}F_{I}$. We calculated it for the 2\,mm atom beam, estimated from the crucible and the orifice geometry, passing through the spherical laser spots on the assumption of each laser power and diameter described in §2.3 and the doppler width of the $T \sim 170$ K potassium atoms. The result was $7.1 \times 10^{-6}$ with both lasers ON and $1.3 \times 10^{-7}$ with only the 405 nm laser ON. The expected improvement ratio of about 60 is a little underestimated probably because of the transport efficiency through the QMS tube. The transport efficiency is supposed to decrease with distance from the axis of the QMS tube, so the actual improvement ratio is thought to be higher due to the larger spot size of the 405 nm laser than that of the 808 nm laser. With these ambiguities, the estimation well reproduces the measured ratio.

### Table I. Involved states for the resonance ionization via the $5p_{1/2}$ excited state. The parity is indicated by appended degree symbols on odd parity terms.

| Number | Electron state | Energy level (cm$^{-1}$) | $g = 2J + 1$ |
|--------|----------------|--------------------------|-------------|
| 1      | $4^2S_{1/2}$   | 0 (ground state)         | 2           |
| 2      | $5^2P_{1/2}$   | 24701.382                | 2           |
| 3      | $3^2D_{3/2}$   | 21536.988                | 4           |
| 4      | $5^2S_{1/2}$   | 21026.551                | 2           |
| 5      | $4^2P_{1/2}$   | 13042.876                | 4           |
| 6      | $4^2P_{1/2}$   | 12985.170                | 2           |

### Table II. Numerical values of each spontaneous emission rate $A_{st}$.

| $A_{st}$ | ($s^{-1}$) | $A_{t}$ | ($s^{-1}$) |
|----------|------------|---------|------------|
| $\Gamma$ | $A_{31}$   | $1.24 \times 10^6$ | $A_{35}$ | $1.56 \times 10^7$ |
| $A_{23}$  | $1.5 \times 10^6$ | $A_{46}$ | $7.9 \times 10^6$ |
| $A_{24}$  | $4.5 \times 10^6$ | $A_{51}$ | $3.87 \times 10^7$ |
| $A_{35}$  | $4.34 \times 10^6$ | $A_{61}$ | $3.82 \times 10^7$ |
| $A_{36}$  | $2.2 \times 10^7$ |       |            |

### 3.3 Isotope discrimination

Isotope discrimination study of potassium has been performed by both EI ionization (§3.3.1) and RIMS (§3.3.2–§3.3.4). Here, the channeltron voltage was the same as that in Fig. 4(a), but the crucible heating current was kept a little lower to 6.00 A, corresponding to the crucible inner temperature of $T \sim 970$ K. The mass resolution of the QMS was set higher at the expense of less sensitivity to reduce the influence of the tail of the adjacent mass peak. During the measurements described in §3.3.2–§3.3.4, the filament for EI ionization was OFF. The natural isotope ratio of potassium is known to be $^{39}\text{K} : 40\text{K} : 41\text{K} = 93.2581\% : 0.0117\% : 6.7302\%$.

#### 3.3.1 Mass spectrum of potassium by EI ionization

In the electron-impact ionization, isotope discrimination is performed only by the mass analysis with the QMS. Figure 6 shows an observed mass spectrum around the potassium mass region. Though the $40\text{K}$ mass peak could hardly be found because of the small abundance, the isotope ratio of $^{39}\text{K} : 40\text{K} = 92.3\% : 7.7\%$ is obtained from the each peak current. The deviation from the natural isotope ratio might be due to the fluctuation of the channeltron current.

The observed peak at $m/z = 44$ is the contribution of CO$_2$ produced by the decomposition of K$_2$CO$_3$ as shown in eq. (1). No atoms nor molecules except for potassium are ionized by the resonance ionization, so this peak is not observed in RIMS.

#### 3.3.2 Hyperfine splitting of potassium

Hyperfine splitting is a splitting of each electron state into multiple energy levels caused by the interaction of the electron spin induced magnetic dipole moment with the magnetic moment of the atomic nucleus. In $^{39}\text{K}$ atoms,
Hyperfine splitting of the 4\(^2\)S\(_{1/2}\) ground state makes two energy levels \(F = 1\) (\(-288.6\) MHz) and \(F = 2\) (173.1 MHz) as shown in Fig. 7, resulting in two observed resonance ionization peaks. Here, \(F\) is the total angular momentum quantum number including nuclear spin. Hyperfine splitting of the 5P\(_{1/2}\) excited state can be relatively ignored.\(^7\)

Figure 8 shows an experimental result of the resonance ionization signal of \(^{39}\)K, \(^{40}\)K, and \(^{41}\)K. The higher peak of \(^{40}\)K at the lower \(V\)\(_{\text{piezo}}\), or the lower laser frequency, corresponds to the \(F = 2\) level of the 4\(^2\)S\(_{1/2}\) ground state of \(^{39}\)K, and the lower peak to \(F = 1\) (see also Fig. 3). The peak current ratio of these two peaks reflects a statistical weight of \(2F + 1\), which is 5 : 3. The same is considered to be true for \(^{41}\)K except for the detailed energy levels of the \(F = 1\) and 2 level of the 4s ground state. The two peaks of \(^{41}\)K are less clearly observed than those of \(^{39}\)K, because the potassium doppler width of about 100 MHz is not negligible compared to the narrower hyperfine splitting width of \(^{41}\)K. The two peaks of \(^{40}\)K correspond to the \(F = 7/2\) level at the lower \(V\)\(_{\text{piezo}}\) and \(F = 9/2\) level at the higher \(V\)\(_{\text{piezo}}\). The peak current ratio of the two peaks of \(^{40}\)K is expected to be 4 : 5.

### 3.3.3 Isotope shift of \(^{41}\)K with respect to \(^{39}\)K

The isotope shift is a slight difference of the transition frequency (wavelength) between the specific pair of the atomic states of two isotopes of the same element. The isotope shift of the 405 nm resonance excitation line of \(^{41}\)K with respect to this line of \(^{39}\)K can be estimated by the observed difference of the piezo voltage \(V\)\(_{\text{piezo}}\) at the peak of the measured channeltron current. Scanning \(V\)\(_{\text{piezo}}\) by hand from 93.5 to 96.0 V, we found the \(^{39}\)K\(^+\) peak current at 94.56 V and \(^{41}\)K\(^+\) at 94.78 V. Both peaks correspond to the resonance excitation line from the \(F = 2\) level of the 4s ground state of each isotope. Figure 9 shows a mass spectrum under each piezo voltage \(V\)\(_{\text{piezo}}\).

The observed difference of the piezo voltage was 0.22 ± 0.01 V, corresponding to the frequency of (4.4 ± 0.2) \times 10^2 MHz or the wavelength of (2.4 ± 0.1) \times 10^{-4} nm. The error is dominated by the reading error of \(V\)\(_{\text{piezo}}\), at the resonant peak and might be improved with a computer control system of it. Taking into account the difference of the splitting width of \(^{39}\)K and \(^{41}\)K 4s ground states as shown in Fig. 7, the isotope shift is calculated to be (3.6 ± 0.1) \times 10^2 MHz. Our result is lower than the precise measurement of this isotope shift using saturation spectroscopy by Halloran et al.,\(^8\)
probably because of the unknown accuracy of the linearity between $V_{\text{piezo}}$ and the laser frequency, in other words, the accuracy of $2\,\text{GHz/V}$ as described in §2.1.

This linearity can be estimated by the known hyperfine splitting width of $^{39}\text{K}$ 4$S_{1/2}$ ground state as seen in Fig. 8. The known splitting width of 462 MHz corresponds to the piezo voltage of 0.19 ± 0.01 V, so the linearity is obtained to be $2.4 \pm 0.1\,\text{GHz/V}$. With this value, the isotope shift is recalculated to be $(4.5 \pm 0.3) \times 10^2\,\text{MHz}$, which is consistent with the data by Halloran et al.8)

As mentioned above, isotopic selectivity can be achieved with a CW laser diode in addition to the mass discrimination by QMS. According to Pulhani et al.,9) the optical isotopic selectivity $\alpha$ for the specific isotope A to the interfering one B is defined as

$$\alpha = \frac{I_A(v_A)/I_B(v_A)}{X_A/X_B},$$

where $I_A(v_A)$ is the intensity of isotope A at its transition frequency $v_A$, $X_A$ is its abundance in the sample, $I_B(v_A)$ is the intensity of isotope B at the transition frequency of isotope A, and $X_B$ is its abundance. Here, the intensity $I$ of each isotope can be replaced by the measured peak channeltron current, so the observed $^{39}\text{K}$ optical isotopic selectivity to $^{41}\text{K}$ is a factor of 5. $^{41}\text{K}$ optical isotopic selectivity to $^{39}\text{K}$ could hardly be estimated because $^{39}\text{K}$ resonance ionization line from the $F = 1$ level of the 4$S_{1/2}$ ground state is close to this $^{41}\text{K}$ line (see Fig. 3). It is necessary to reduce the effect of the doppler width for the improvement of the optical isotopic selectivity.

The isotope ratio of $^{39}\text{K}$ : $^{41}\text{K}$ = 93.1% : 6.9% is estimated from the peak current of $^{39}\text{K}$ at $V_{\text{piezo}} = 94.56\,\text{V}$ and $^{41}\text{K}$ at $V_{\text{piezo}} = 94.78\,\text{V}$ in Fig. 9, which is close to the natural isotope ratio and the result of EI ionization described in §3.3.1.

3.3.4 Mass spectral peak of $^{40}\text{K}$

$^{40}\text{K}$ is the naturally-occurring radioactive potassium isotope which has an abundance of 0.0117%.6) In this work, the mass peak of $^{40}\text{K}$ has also been observed as shown in Fig. 10 with a setting of better mass resolution (leading to a little lower sensitivity) for the QMS as well as fine-tuned piezo voltage to about 95 V. This peak is thought to be the resonance excitation signal from the $F = 9/2$ lower level of the 4$s$ ground state because of the higher piezo voltage, in other words, higher frequency of the observed line than $^{39}\text{K}$ or $^{41}\text{K}$ (see Fig. 7).

Comparing the peak current at $m/z = 39$ and 40, $^{40}\text{K}$ optical isotopic selectivity to $^{39}\text{K}$ is estimated to be about 7. Taking into account the fact that the isotopic selectivity increases with additional resonance excitation processes, higher selectivity could be achieved by resonance ionization through multiple excited states.

4. Future Prospect

Our resonance ionization mass spectrometer is quite effective for the trace element analysis because of its low noise level of the channeltron detector as well as insensitivity to isobaric interferences. Especially, it can be applicable to the contamination assessment on the surface of the semiconductor wafer.

ICP–MS is mainly used in this field conventionally, however it suffers from argon plasma interferences with mass region around 40, resulting in relatively worse detection limits of potassium ($^{39}\text{K}$) and calcium ($^{40}\text{Ca}$) than other elements.

The detection efficiency of the present system is limited by the power of 808 nm ionizing laser. Therefore, we are planning to increase the 808 nm laser power by a factor of 20 using an Apollo Instruments model FL-60. We expect a detection limit of potassium (K) of comparable to or even better than that of ICP–MS with our improved system.

The laser diode is a good device to use for the resonance excitation because of its narrow linewidth and relatively low price. However, it is not applicable to the analysis of other chemical elements for the limited variable wavelength range. For the contamination assessment of a variety of impurities on the wafers, a variable wavelength dye laser can be used at a higher cost.

5. Conclusions

Trace element analysis of potassium gas atoms has been performed by our own resonance ionization mass spectrometer consisting of two laser diodes for resonance ionization and QMS for mass analysis. In this work, the optical fiber output of each laser diode is fixed to the viewport of the QMS to avoid misalignment of the laser spot due to vibration of the vacuum system. The use of the fiber output makes us easy to optimize the optical system without any additional mirrors or optical tables. The overall detection efficiency is currently estimated to be $7 \times 10^{-8}$.

Taking advantage of the narrow linewidth of the 405 nm laser diode, isotopic discrimination test has also been performed with a high resolution QMS setting to verify the isotope shift and the optical isotopic selectivity. The isotope shift between $^{39}\text{K}$ and $^{41}\text{K}$ in the 405 nm resonance excitation line is estimated to be $(4.5 \pm 0.3) \times 10^2\,\text{MHz}$ compared to the known hyperfine splitting width of $^{39}\text{K}$ 4$S_{1/2}$ ground state. The obtained optical isotopic selectivities of $^{39}\text{K}$ to $^{41}\text{K}$ and $^{40}\text{K}$ to $^{39}\text{K}$ are about 5 and 7, respectively. A clear hyperfine splitting of the 4$s_{1/2}$ ground level was observed in each potassium isotope.

We are planning to apply RIMS to the contamination assessment on the surface of the semiconductor wafer. The
The detection limit of potassium impurities can be improved to be comparable to or even better than that of a conventional method of ICP–MS by increasing the 808 nm laser power by a factor of 20. Also, a wavelength-tunable dye laser to cover the wide range of resonance excitation wavelength enables us to perform contamination assessment of a wide variety of impurities in addition to potassium.

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