Surface Ionization of Na- and K- Compounds by a Single Filament Mass Spectrometry

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The surface ionization phenomena of Na- and K- compounds are studied by applying the samples directly on a tungsten ionization filament. The transient variations and the steady state characteristics of the ion emission seem to be due to the sample supply taking place by diffusion along the hot filament surface to the ionization spots, and hence it is supposed almost impossible to expect the precise quantitative mass analyses of sample compounds by means of the surface ionization of this sort.

1. Introduction

In a previous paper¹⁾ concerning a mass spectrometric analysis of solids by the surface ionization, we presented the abnormal and uncontrollable variations of K^+ ion current emitted from KCl sample which was applied directly on a tungsten ionization filament. In the present article, a few additional phenomena observed on the same subject and on the mass analyses of mixture samples are presented together with some considerations.

The surface ionization is an interesting phenomenon, but it depends on too many

delicate conditions to be studied readily. The well-known equation of Saha-Langmuir²⁾ gives the ratio of numbers of ionized and neutral particles provided some rather strict conditions are fulfilled: they are 1) the hot metal surface is clean and homogeneous, 2) the flux of the particles impinging upon the surface from the surrounding space is steady, 3) there exists an equilibrium between the adsorbed and desorbed particles on the hot surface, 4) the temperature of hot surface is uniform, etc. All of these conditions must be satisfied to study the surface ionization closely.

In a routine mass spectrometry of solids

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by the surface ionization, especially by using a single hot filament which is coated directly with the sample to be ionized, the situation is different from that to which the Saha-Langmuir equation can be applied without any modification. The present article will show that the transient variations of the ion emission may be due to the transient variations of the surface coverage on the ionization spots of the filament surface with the sample particles which are supplied by diffusion along the hot surface, and that in the steady state also what almost determines the ion emission characteristics might be the process of the sample supply of this mode.

2. Instruments

2.1. Vacuum diode arrangement

To study the ion emission from the sample salt on a hot filament, a vacuum diode circuit shown in Fig. 1 was arranged. The plate which acted as a collector of emitted ions or electrons was a nickel cylinder of 6 mm in diameter and 4 mm in

Fig. 1. Vacuum diode arrangement.

length. Two guard cylinders on both sides of the plate worked to keep the electric field inside the plate uniform and to prevent the currents from coming out of the ends of the filament.

2.2. Mass spectrometer

The mass spectrometer used was a stereo-convergent type³⁾ of 200 mm in ion-path radius in a sector shaped magnet with 45° apex angle. The central ion path goes into and out of the magnet obliquely to its boundaries and deflects 75°. The scheme of the ion source is shown in Fig. 2. To stabilize the temperature of the active filament, another identical bare filament was connected in series as an auxiliary

Fig. 2. Ion source.

Fig. 3. Auxiliary filament for temperature stabilization.

filament as shown in Fig. 3, and the electron emission from the latter was stabilized by an ordinary emission regulator circuit. This was the method proposed previously⁴⁾ and Fig. 4 shows how the ion current emitted from the active filament was stabilized by applying this temperature regulation arrangement.

Fig. 4. Regulated and unregulated ion currents.

2.3. Filament used and sampling

Throughout the present experiment, the filament used was a tungsten ribbon of 0.025 mm thick and 0.75 mm in width. Before applying to the experiment, the filament was pre-heated in a high vacuum to desorb out the possible impurities. The filament temperature with every filament current had been measured beforehand by an optical pyrometer.

An active filament surface was coated with the sample salt by putting a drop of aqueous solution on and drying up by a heating lamp.

3. Ion emission study of KCl by a vacuum diode arrangement

In the present experiment, the polarity

of the plate voltage V_P shown in Fig. 1 was designated as positive. The filament current will be denoted as I_f .

3.1. Time-variations of K^+ ion current

3.1.1. Effect of sudden change of V_P

($I_f = \text{const.}$)

A sudden increase of the plate voltage caused an abrupt increase of the ion current followed by an exponential-like decay as seen in Fig. 5. The semi-logarithmic plot

Fig. 5. Effect of sudden change of V_P .

in Fig. 6 shows that this decay was exponential but with a steeper initial decrease in current. This mode of decay was observed at every experiment independently of the initial condition of the transient, although the slope of the decay was not necessarily of the same value.

Figure 7 shows the effect of an interruption of V_P on the ion current during the period of its transient decrease, and this suggests some go-back of the transient

Fig. 6. Semi-log plot of Fig. 5.

Fig. 7. Effect of sudden interruption of V_p .

process. This and the foregoing exponential characteristics of decay seem to be explained by the change of the coverage on the hot surface with the ionized atoms K^+ . The exponential decrease of the current with time would be due to the reduction of the surface coverage with ions, while during the interruption of V_p the coverage might have revived somewhat.

3.1.2. Effect of sudden change of I_f ($V_p = \text{const.}$)

The effects of sudden change of the filament heating current I_f on the emitted ion currents are shown in Fig. 8. Figures 8(a) and (b) show the resulting variations of ion currents when the current I_f were suddenly increased; Fig. 8(a) was that observed when I_f was rather low, while in Fig. 8(b) I_f was higher. In both cases, except the initial zigzag variations of the currents, the current decreased or increased exponentially, and these phenomena also seemed to be due to the variations of the surface coverage with time. The difference between the cases of Figs. 8 (a) and (b) can be explained by the difference of the rate of the particle immigration to the ionization spots on the surface. In the case of lower heating current, the rate of particle supply would be low, while for the higher supply would be high, and thus resulting in the decrease or increase of the surface coverage to attain to the new equilibria.

Figure 8 (c) presents the effect of an interruption of I_f on the ion current. During the period of interruption, the transient process seemed to be "frozen" and the surface coverage with ions remained

constant. Applying I_f again, the process started from the same situation where it had been stopped.

The zigzag variation of the ion current which occurred immediately after a sudden increase of the filament current I_f was observed almost every transient of this sort, and presumably, this was due to the cooling effect which made the ion current drop steeply after the burst of starting current.

3.2. Ion- and electron emissions

The plate currents of the diode obtained by varying the plate voltage V_p are shown in Fig. 9. Every datum in the following experiments was that taken in an equilibrium state and thus has no connection with that mentioned above. The positive current I_+ was the ion current of K^+ emitted and the negative current I_- was, because of its predominant intensity, the thermoelectronic emission current. Figure 9 shows that the electron current overwhelmed the initial positive current up to +2.4 volts of V_p . Figure 10 and 11 show the family of electron and ion currents measured with different filament temperatures. These figures show the distributions of the initial energies of the emitted particles. From Fig. 10, the contact potential of the present system was estimated to be about 0.9 volts.

According to the equation

Fig. 8. Effect of sudden change of I_f .

Fig. 9. Ion and electron emissions in diode.

$$\log \frac{I_-}{T^2} = \log A_- - 0.43 \frac{\phi_-}{kT}$$

the Richardson plot of the emitted electron current I_- in Fig. 10 is drawn in Fig. 12,

Fig. 10. Emission currents I_+ v.s. temperatures.

Fig. 11. Emission currents I_+ v.s. temperatures.

and this gives the effective work function ϕ_- for I_- of 1.48 eV, which suggests the emission spots of the tungsten surface being covered with monatomic layer of K^+ ions. The semi-logarithmic plot of the emitted ion current I_+ in Fig. 11 is presented also in Fig. 12 in accordance with the equation

$$\log I_+(K) = \log A_+ - 0.43 \frac{\phi_+(K)}{kT}$$

and the effective work function $\phi_+(K)$ for $I_+(K)$ is evaluated as 3.34 eV.

There occurred no reasonable idea to explain the deviations of upper points in Figure 12; probably there were some unknown troubles in the experiment.

Fig. 12. Semi-log. plots of emission currents.

4. Ion emission study of NaCl-KCl mixture by a mass spectrometer

In the following experiments and discussions, the ion-repeller and draw-out voltages V_R and V_D are designated as shown in Fig. 13.

Fig. 13. V_R and V_D defined for ion source.

4.1. Ion- and electron emissions

Connecting the draw-out plate to the ionization chamber in the ion source, a diode was formed with the plate voltage V_R . Figure 14 shows the ion- and electron emission currents of this diode connection,

Fig. 14. Ion- and electron emissions in ion source.

and the pattern was the same as that of Fig. 9 as expected. In this case, the repeller voltage over 10 volts was needed to get a saturated ion current; this voltage, however, was rather higher than the adequate values for an ordinary operation of an ion source.

4.2. Dependence of mass spectra on the voltages V_R and V_D

A mixture sample of KCl and NaCl in 500 : 1 mole ratio was applied on the ionization filament in the ion source. Figures 15 and 16 show the dependence of mass spectra on the voltages V_R and V_D , respectively. The arrangement composed of ionization filament, ionization chamber, and ion draw-out plate can be assumed as forming a triode, and the electric field acting on the filament can be estimated by its equivalent diode plate voltage V_F given as

$$V_F = V_R + \frac{V_R + V_D}{\mu} \approx V_R + \frac{V_D}{\mu}$$

Fig. 15. Dependence of mass spectra on V_R .

Fig. 16. Dependence of mass spectra on V_D .

where μ is the amplification factor of the assumed triode. Figure 15 presents an unreasonable result that the preferable ion emissions were obtained in the negative values of V_R , but this can be understood by considering a high positive voltages of V_D and resulting equivalent positive plate voltage V_P , although such a potential distribution would not be desirable in most cases.

Figure 15 reveals that there exists a mass discrimination effect in the ion source due to the repeller voltage V_R , while Fig. 16 shows none for the draw-out voltage.

4.3. Dependence of mass spectra on the filament temperature

Figure 17 shows the results of mass analyses. Figure 18 is the semi-logarithmic plots of the ion currents of Na^+ and K^+ in Fig. 17, which shows that the ion currents can be expressed as

$$I_+ = I_0 \exp\left(-\frac{\phi_+}{kT}\right) \quad \text{.....(1)}$$

Fig. 17. Dependence of mass spectra on T .

Fig. 18. Semi-log. plots of ion currents.

and from the plots, the effective work functions for the ions are given as

$$\phi_+(\text{Na}) = 4.14 \text{ eV} \dots\dots\dots(2)$$

and

$$\phi_+(\text{K}) = 3.34 \text{ eV} \dots\dots\dots(3)$$

the latter is the same value as that presented in Sec. 3. 2. The ratio of the ion currents K^+/Na^+ in Fig. 17 varies thus exponentially with the filament temperature.

5. Discussions and conclusion

As pointed out in the introduction of this article, it would be rather unreasonable to try to apply fine theoretical discussions to the present results of a routine mass spectrometry where there exists no evidence that the surface of the hot filament is clean and homogeneous and that the sample applied on this surface is absolutely uniform. The problems arose just from this patchy surface where the sample atoms and ions could coexist in a variety of states and concentrations.

Concerning the transient phenomena observed on the ion emission, some considerations were already given in every section, where the variations of ion currents were attributed to the variations of the surface coverage on the ionization spots with adsorbed particles. Here, however, the variations of the ion currents which we put in question were those that showed the exponential feature and hence could be called as regular. The variations which often troubled us more were quite irregular and almost random ones especially when the sample on a hot filament was new and excess in amount, and probably those would be due to the unstable sticking of the sample particles on a filament

surface.⁵⁾ Thus, the problem to be discussed in the following is the surface ionization in its steady state which would be essential in the routine mass spectrometric analyses of solids.

Suppose the constant flux n of the particles impinging upon the hot metal surface and the emitted fluxes n_0 of neutral and n_+ of positively ionized particles in a equilibrium state. The situation is hence

$$n_0 + n_+ = n \dots\dots\dots(4)$$

and the Saha-Langmuir equation gives the degree of ionization as

$$\alpha = \frac{n_+}{n_0} = A \exp \left(\frac{\phi - V}{kT} \right) \dots\dots\dots(5)$$

where ϕ is the work function of the metal, V the ionization potential of the adsorbed particles. A is the proportional constant which includes the statistical weights and the reflection coefficients of the emitted atoms and ions. However, as A is not a function of T , it can be assumed unity hereafter to simplify the present discussion. It would also be allowable not to take into account the Schottky effect here because of the weak electric field on the hot surface, and this would be usually the case in an ordinary mass spectrometry.

Now, the ion current I_+ observed in our experiments is

$$I_+ = n_+ e$$

and from Eqs. (4) and (5), this yields

$$I_+ = \beta n e = \frac{\alpha}{1 + \alpha} n e \dots\dots\dots(6)$$

where β defines the ionization coefficient, e the charge of an ion. The postulate from

which Eqs. (5) and (6) are concluded is that the sample particles on a hot filament are supplied from the surrounding space in a constant flux, that is, the value of n in Eq. (6) is a constant. In our experiments, however, the sample particles are supposed to be supplied by diffusion along the surface, and the supply flux can therefore be expressed as

$$n = -D \cdot \left(\frac{\partial n}{\partial x} \right) \dots\dots\dots (7)$$

considering x direction only for simplicity. D is the diffusion coefficient and

$$D = D_0 \exp\left(-\frac{E_d}{kT}\right) \dots\dots\dots (8)$$

where E_d is the activation energy of diffusion. From Eqs. (6), (7), and (8) we have

$$\begin{aligned} I_+ &= -D_0 \left(\frac{\partial n}{\partial x} \right) \exp\left(-\frac{E_d}{kT}\right) \cdot \frac{\alpha}{1+\alpha} e \\ &= \text{const} \cdot \exp\left(\frac{\phi - E_d - V}{kT}\right) \cdot \frac{1}{1+\alpha} \dots\dots (9) \end{aligned}$$

The work function ϕ of tungsten is 4.52 eV in average,⁶⁾ and the ionization potential V of Na and K are 5.14 eV and 4.34 eV, respectively,⁷⁾ and hence

$$\alpha(\text{Na}) = \exp\left(-\frac{0.62}{kT}\right) \dots\dots\dots (10)$$

and

$$\alpha(\text{K}) = \exp\left(\frac{0.18}{kT}\right) \dots\dots\dots (11)$$

5.1. Ionization of Na

For $T=2,000^\circ\text{K}$, say, $kT=0.17$ eV and from Eq. (10), $\alpha(\text{Na})=0.03$ and thus can be omitted from the denominator of Eq. (9) in the temperature range of this order.

The ion current of Na^+ can therefore be expressed as

$$I_+(\text{Na}) = \text{const} \cdot \exp\left(\frac{-0.62 - E_d}{kT}\right) \dots\dots\dots (12)$$

On the other hand, as given in Eq. (2), Sec. 4.3, the observed effective work function $\phi_+(\text{Na})=4.14$ eV, i. e.,

$$-0.62 - E_d = -4.14$$

or

$$E_d(\text{Na}) = 3.52 \text{ eV} \dots\dots\dots (13)$$

5.2. Ionization of K

For $T=2,000^\circ\text{K}$, for instance, $\alpha(\text{K})=2.88$ and cannot be neglected in Eq. (9). Thus, we obtain for K^+ ions

$$\begin{aligned} I_+(\text{K}) &= \text{const} \cdot \exp\left(\frac{0.18 - E_d}{kT}\right) \cdot \\ &\quad \frac{1}{1 + \exp\left(\frac{0.18}{kT}\right)} \dots\dots\dots (14) \end{aligned}$$

Equating this and the experimental result expressed in Eqs. (1) and (3) gives

$$\begin{aligned} \exp\left(\frac{0.18 - E_d}{kT}\right) &= \exp\left(-\frac{3.34}{kT}\right) \cdot \\ &\quad \left[1 + \exp\left(\frac{0.18}{kT}\right) \right] \end{aligned}$$

and from this

$$\begin{aligned} E_d(\text{K}) &= 3.52 - kT \ln\left[1 + \exp\left(\frac{0.18}{kT}\right) \right] \text{ eV} \\ &\dots\dots\dots (15) \end{aligned}$$

The second term on the right ranges from 0.19 to 0.23 eV for T of 1,000 to $2,000^\circ\text{K}$.

In the above discussions, the possible effects of the temperature on the ion emission are collectively attributed to the acti-

vation energy E_d of diffusion, and hence E_d might be called as "appearance" in the present consideration. However, since the values of E_d obtained for Na and K can be regarded as reasonable referring to some other results,^{8,9)} it could be concluded that the sample supply to the ionization spots on a hot filament by the surface migration plays a leading part in the present ion emission, and, because of this, it seems very hard or even impossible to expect the precise quantitative mass analyses of the components of a mixture sample.

The present study was promoted by the difficulties encountered in the course of routine surface ionization mass spectrometry using a tungsten ribbon filament and the samples of alkali metal chlorides. Kawano and Inouye¹⁰⁾ reported the surface ionization of alkali metal iodides on a heated platinum coil and obtained the stable and reproducible results, and this suggests to us the need of further studies on the material of the hot filament used and the

compounds of the sample with which the filament is coated.

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Keywords

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