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STUDY OF ADSORPTION OF POTASSIUM ATOMS ON A MICA SURFACE BY MEANS OF MOLECULAR BEAMS

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The process of the deposition of potassium atoms on a mica surface is observed by means of molecular beams. The sticking coefficient changes with the deposition time. The observed change is discussed by a simple rate theory on assumptions similar to those of the "BET" model.

Deposition of metal vapors on solid surfaces has been investigated by various methods (by means of electron microscope, microbalance, electric resistance, etc.). However, the experimental studies on the initial stage of deposition seem to be insufficient because of the lack of sensitivity in measuring small amount of the deposit.

In these few years[1] we have studied the spatial distribution of potassium atoms scattered from various surfaces using well defined atomic beams, and the cosine distributions of the scattered beams were observed for many cleaved alkali halide surfaces. Recently, in the course of experiments on cleaved surfaces of mica we found an interesting phenomenon with respect to vapor deposition. In this paper the experimental results will be shown and discussed.

EXPERIMENTAL

An apparatus was constructed for the purpose of measuring the spatial distribution of potassium atoms scattered from crystal surfaces. It consisted of three chambers evacuated differentially by oil diffusion pumps (see Fig.1). Potassium beams effused from an oven in the chamber 1 passed through the chamber 2 and impinged on a target in the chamber 3. The beams scattered from the target were detected with a surface ionization qauge rotatable around the target. The distance between the detector and the target surface was 37 mm. The target holder located at the center of the chamber 3 could also be rotated on its axis and moved up and down. Thus, the incident angles of the beam could be changed and the target could be removed from the beam path. The target holder could be heated by a heater or cooled with cold nitrogen gas. The surface temperatures were measured by a thermocouple contacted to the surface.

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In the present experiment, cleaved surface of mica (muscovite) were used as a target and heated to 440°C in vacuum prior to measurements. To investigate the spatial distribution the signal of the scattered beam was measured at each angle by on-off of the beam flag. To measure the change of the intensity of the scattered beam with time, the incident angle of the beam was kept at 45° and the detector was set in the normal direction of the surface. Typical flux of incident beam was about 3×10^{12} atoms/cm^2 sec, and the surface area exposed to the beam was 5.22×10^{-2} cm^2. The constancy of the intensity of the incident beam was checked before and after each run of the experiments. The pressure in the chamber 3 was 2×10^{-8} Torr during the run.

EXPERIMENTAL RESULTS

In the case of the stationary scattering on cleaved surfaces of LiF, KCl, and mica in higher temperatures, the spatial distributions of the scattered beam obeyed usually the cosine law of Knudsen. The typical spatial distributions are shown in Fig.2. From the results it may be reasonable to consider that the main process of the scattering was the re-evaporation after the adsorption of the incident atoms. Therefore, when the spatial distribution could not measured due to the change of signal intensity during a run, we assumed the cosine distribution at lower temperatures. Figure 3 shows the time dependence of the intensity of the beam scattered from a surface of mica at 315 K. From such measurements, the number of atoms staying on the surface at time t, $\sigma(t)$, can be determined by

$$\sigma(t) = \int_0^t I\,dt - \int_0^t \int_\Omega R(\theta,\phi;t)\,d\omega\,dt, \qquad (1)$$

where I (atoms cm^{-2} sec^{-1}) is a flux of incident beam, $R(\theta,\phi;t)$ the number of outgoing atoms per second in the solid angle $d\omega$ of the direction (θ,ϕ), and Ω indicates the integration over the hemisphere. Assuming the cosine distribution for $R(\theta,\phi;t)$, $\sigma(t)$ were evaluated by the equation (1) and the evaluated results are shown in Fig.4. On the surface at a higher temperature such as 653 K, $\sigma(t)$ was stationary after a short exposure time, but at lower temperatures $\sigma(t)$ increased monotonically with exposure. The monotonically increasing curve of $\sigma(t)$ had a point of inflection which corresponded to the maximum in Fig.3. The values σ for the inflection points are 4.1×10^{14} atoms/cm^2 at 315 K and 3.6×10^{14} atoms/cm^2 at 273 K, respectively. These values are nearly equal to the number of the potassium atoms in monolayer, i.e., 4.50×10^{14} atoms/cm^2, which was evaluated from the density of liquid potassium. To interpret the phenomenon, let us introduce the apparent sticking coefficient S(t) defined as

$$S(t) = \frac{d\sigma(t)}{dt} \Big/ I. \qquad (2)$$

Figure 5 shows the change of the sticking coefficient vs. exposure time calculated from the results shown in Fig.4. The inflection point of the σ curve corresponds to a minimum in the sticking coefficient curve. The position of the minimum suggests that the different processes dominate the adsorption phenomenon on the mica before and after the minimum.

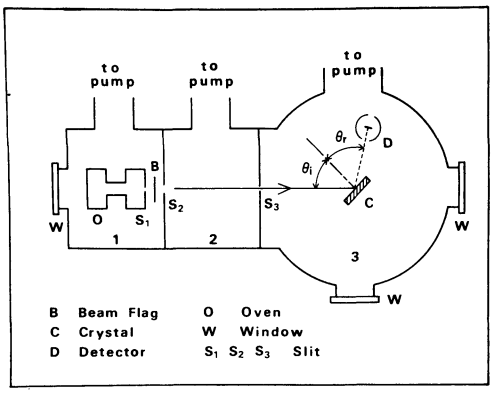

Fig. 1. Schematic drawing of the apparatus.

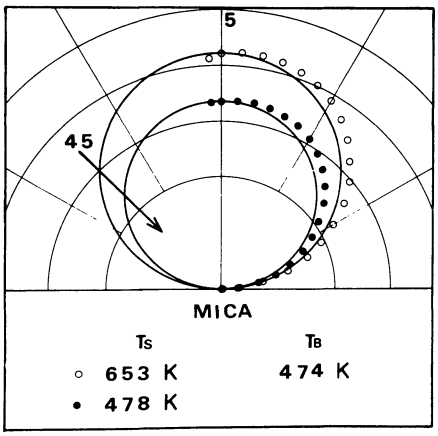

Fig. 2. Spatial distributions of potassium atoms scattered from a mica surface. The solid circles indicate the cosine law.

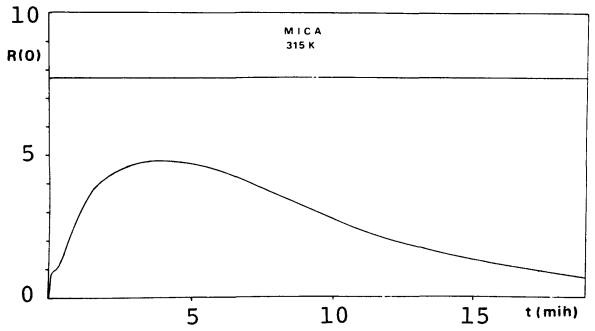

Fig. 3. Scattered beam intensity vs. exposure time.

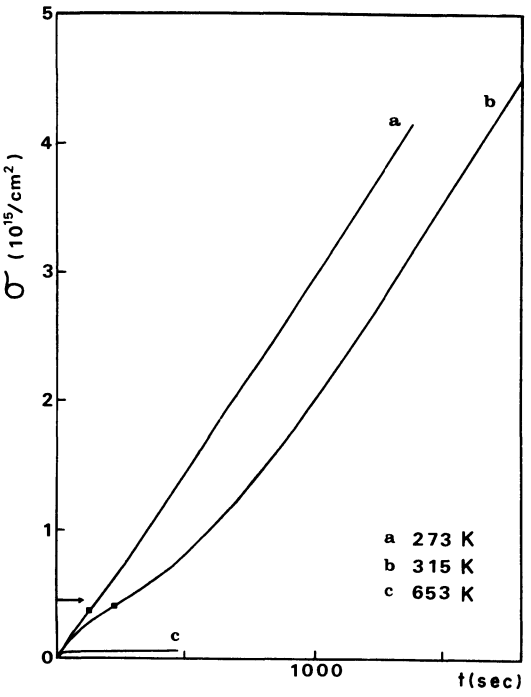

Fig. 4. The number of adsorbed atoms vs. exposure time.

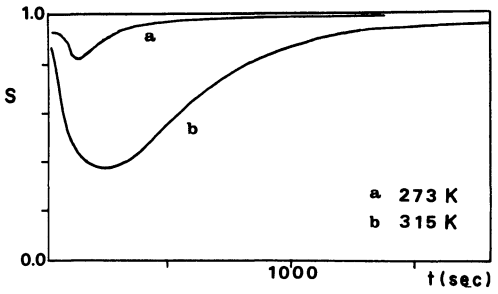

Fig. 5. Change of the sticking coefficients vs. exposure time.

THEORY

Let us consider a simple model similar to the "BET" model to interpret the present phenomenon qualitatively. The model assumes that an impinging atom on the surface is adsorbed at the site whether it is bare or not. The number of the sites on the surface is N in unit area. Migration of an adsorbed atom on the surface is neglected here and each adsorbed atom has a finite life-time before desorption. The mean life-time of the atoms adsorbed in the first layer is τ_1, in the second layer τ_2, and in the third layer τ_3, etc. The interaction of atoms adsorbed in different sites is neglected in the present model. Now, express the number of bare sites by n_0, the number of sites filled the first layer by n_1, and that filled the second layer by n_2, etc. According to the above model, a simple rate theory for adsorption kinetics can be given by a series of following basic equations,

$$\begin{aligned}
\frac{dn_1}{dt} &= \frac{I}{N}(n_0 - n_1) - \frac{n_1}{\tau_1} + \frac{n_2}{\tau_2}, \\
\frac{dn_2}{dt} &= \frac{I}{N}(n_1 - n_2) - \frac{n_2}{\tau_2} + \frac{n_3}{\tau_3}, \\
&\text{- - - - - - - -} \\
\frac{dn_i}{dt} &= \frac{I}{N}(n_{i-1} - n_i) - \frac{n_i}{\tau_i} + \frac{n_{i+1}}{\tau_{i+1}}, \\
&\text{- - - - - - - -}
\end{aligned} \tag{3}$$

where $N = n_0 + n_1 + n_2 + \text{------} + n_i + \text{------}$. To solve the infinite series of linear differential equations, we must set a final equation in the series of equations (3). Therefore, the adsorption above the Lth layer was neglected. Another assumption is to put $\tau_2 = \tau_3 = \text{-------} = \tau_L$, which is reasonable for a similar nature of the interaction between atoms above the first layer (potassium-potassium interaction in the present experiments). For such a case, the series of equations (3) is simplified as

$$\begin{aligned}
\frac{dn_1}{dt} &= \frac{I}{N}(n_0 - n_1) - \frac{n_1}{\tau_1} + \frac{n_2}{\tau_2}, \\
\frac{dn_2}{dt} &= \frac{I}{N}(n_1 - n_2) - \frac{1}{\tau_2}(n_2 - n_3), \\
&\text{- - - - - - - -} \\
\frac{dn_L}{dt} &= \frac{I}{N}n_{L-1} - \frac{n_L}{\tau_2}.
\end{aligned} \tag{4}$$

Here, defining a sticking coefficient S as

$$S \equiv \sum_{i=1}^{L} i\frac{dn_i}{dt} \Big/ I, \tag{5}$$

we can obtain the formula below from the set of equations (4)

$$S = 1 - \frac{n_1}{\tau_1 I} - \frac{1}{\tau_2 I}\sum_{i=2}^{L} n_i \ . \qquad (6)$$

When the number of adsorbed (deposited) atoms goes to infinity with the time of exposure to the beam, the sticking coefficient is given by

$$\lim_{t\to\infty} S = 1 - \frac{N}{\tau_2 I} \ , \qquad (7)$$

where we assumed $\lim_{t\to\infty} n_1(t) = 0$ and $\lim_{t\to\infty}\sum_{i=2}^{L} n_i = N$. Using Eq.(7), we could estimate τ_2 from the final values of S on the right-hand side of the minima of the sticking coefficient curves in Fig.5. The values τ_2 were 1.44×10^4 sec at 273 K and 3.15×10^3 sec at 315 K, respectively.

According to the Frenkel's equation

$$\tau_i = \tau_i^o \exp(E_i/kT) , \qquad (8)$$

we can estimate the desorption energy E_2 from the determined life-time τ_2. Assuming pre-exponential factor $\tau_2^o = 1 \times 10^{-13}$ sec, the desorption (sublimation) energy E_2 of potassium atoms was evaluated for the present values τ_2 as about 1 eV. This value is nearly equal to the sublimation energy of potassium atoms, 0.94 eV, given in a literature[2].

For the case of the deposition of metal vapor on an alkali halide or a mica surface such as the present system, the interaction energy E_1 between the adsorbed atom and the surface atom probably may be smaller than the sublimation energy E_2 of the metal. Therefore, τ_2 will be longer than τ_1. Assuming various values of τ_1 which are shorter than the evaluated τ_2, the set of linear differential equations ending with L=9 were solved numerically by the standard Runge-Kutta-Gill method. The used computer was a FACOM 230-60 in Kyoto University. The sticking coefficients calculated by Eq.(6) are shown in Fig.6 and Fig.7. The each theoretical curve has a minimum as in the experimental results.

DISCUSSION

A deep minimum of the sticking coefficient as seen at 315 K in Fig.5 could not be interpreted by the above theory. One of the reasons may be attributed to the neglection of the horizontal interaction between the atoms adsorbed on different sites. Therefore, the simple theory might be improved by the assumption of $\tau_2 < \tau_3 < \tau_4 <$------, because the horizontal interaction became effective with increasing the number of the adsorbed atoms. However, if the number of parameters increases, other difficulties for the determinations of the parameters will be added to the calculation. Considering the horizontal interaction more completely, each differential equation in the series of equations (3) will be non-linear and more complicated.

When a surface temperature is high, the migration of the adsorbed atoms on the surface must be considered in the model. However, τ_1 at higher temperature is sufficiently small and the deposition of the metal vapor will not proceed due to

the small rate of formation of the first layer. In such a case, long-lived polymers formed accidentally on the surface will become nuclei to which the migrating atoms aggregate.

Under the thermal equilibrium the left terms in the set of equations (4), dn_1/dt, dn_2/dt, etc. can be put to zero. Thus, the formula equivalent to the Lth "BET" equation can be obtained as

$$\frac{v}{v_m} = \frac{\sum_{i=0}^{L} in_i}{\sum_{i=0}^{L} n_i} = \frac{cx\{ 1 - (L + 1)x^L + Lx^{L+1}\}}{(1 - x)\{ 1 + (c - 1)x - cx^{L+1}\}}, \qquad (9)$$

where v is the total volume of the adsorbed atoms, v_m the volume of the monolayer, $x = \tau_2 I/N$, and $c = \tau_1/\tau_2$.

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2) A. N. Nesmeyanov, "Vapor Pressure of the Chemical Elements" (English edition), R. Gary, Ed., Elsevier Publ. Co., Amsterdam (1963), p432.

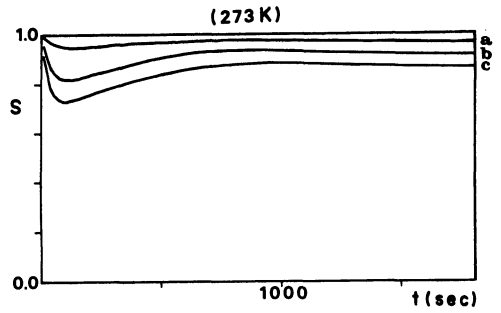

Fig.6. Results of the calculation of the sticking coefficient for 273 K. Values used for τ_1 are 1000 sec (a), 200 sec (b), and 100 sec (c), respectively.

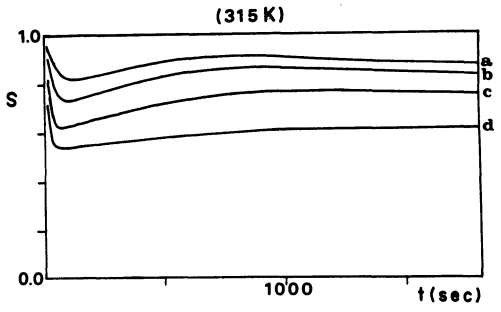

Fig.7. Results of the calculation of the sticking coefficient for 315 K. Values used for τ_1 are 200 sec (a), 100 sec (b), 40 sec (c), and 10 sec (d), respectively.

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