Laser Original

On the Mechanism of Laser-Induced Suppression of Xe Sublimation from BCl_3 -Xe Solid Mixtures

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The sublimation rate of Xe from a BCl_3 -Xe solid mixture with low dilution at about 70 K, is suppressed more than 30% by exciting the BCl_3 ν_3 vibration. A possible explanation for this phenomenon is presented. Larger volatility of Xe than that of BCl_3 causes the formation of a dense BCl_3 layer at the surface of the solid. To sublime, Xe should diffuse through this layer. The diffusion of Xe in BCl_3 would probably be inhibited by the increase of vibrational amplitude of BCl_3 molecules. It is shown in terms of probabilities that the small increase of interaction cross section between Xe and BCl_3 can significantly decrease the Xe diffusivity in the BCl_3 layer.

1. Introduction

In our experiments on laser chemistry with rare gas solids, an unexpected effect has been observed^{1,2)}. Under a specific condition, the sublimation rate of Xe from a BCl_3 -Xe solid mixture on a Ge substrate, is suppressed more than 30 % by exciting the BCl_3 ν_3 vibration with a cw CO_2 laser. In the experiments, laser irradiations of 120 s were repeated at intervals of 120 s. At the end of each irradiation, the temperature of the substrate rose at least 0.5 K. This temperature rise corresponds to about 25 % increase in Xe sublimation pressure³⁾. Therefore, it would be natural to expect that the sublimation rate of Xe should increase by laser irradiation.

Some discussions about the situation of the solid sample were devoted previously^{1,2)}. The volatility of Xe is extremely larger³⁾ than that of BCl_3 ⁴⁾, and the irradiation cell had been evacuated

continuously with an oil diffusion pump. Consequently, Xe sublimated fractionally from the solid mixture to form a thin and dense layer of BCl_3 at the surface of the sample. Once the layer is formed, Xe must diffuse through the BCl_3 layer from inside of the sample to the surface, to sublime. It was suggested that the diffusion of Xe in the BCl_3 layer might be inhibited by the excitation of BCl_3 vibration.

It should be mentioned that the decreased pressure of Xe by laser irradiation recovers when the laser beam is shut off. Therefore, the change of BCl_3 layer which suppresses the sublimation seems to be related directly to the vibrational excitation of BCl_3 itself, and not to such a permanent one as configurational change through chemical reaction or thermal melting. To see whether the suppression is due to the reorientation of BCl_3 molecules by laser irradiation, we have varied the angle of incidence in an experiment. And as shown in Fig. 1, it has been found

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Fig. 1 A result of successive cw CO₂ laser irradiations with a 2.5 W 10P(20) line, to see the effect of the angle of incidence to the sample surface, on the magnitude of suppression ($1-p^*/p$) of Xe sublimation, where p and p^* stand for the vacuum pressure in the system before and after irradiation, respectively.

that this is not the case. Thus, we wish to propose that the suppression is probably due to the increase in apparent molecular size of BCl₃ by vibrational excitation. The expansion of BCl₃ molecules will increase the cross section of interaction between Xe and BCl₃, thereby the diffusivity of Xe in the layer may decrease.

In order to substantiate the proposed mechanism, it will be required to show that a small increase in molecular size can significantly decrease the Xe diffusivity in the BCl₃ layer, since the expansion of a molecule by vibrational excitation is estimated to be a few percent. The purpose of this paper is to show theoretically that the diffusion of gas molecules in solid is possibly inhibited by the vibrational excitation of constituent molecules of the solid. Consequently, the mechanism of the suppression of sublimation by laser irradiation can be elucidated by the decrease of the diffusivity of Xe in the BCl₃ layer formed at the surface of the solid mixture.

2. Theoretical

First, we investigate the relation between the Xe sublimation rate and the Xe diffusivity in a BCl₃ layer. As mentioned above, BCl₃ molecules should form a thin and dense layer at the surface of the remaining BCl₃-Xe solid mixture. We shall locate the origin of coordinates at the inner boundary of the BCl₃ layer, and take the x -axis outward in the direction perpendicular to the surface. The effective thickness and the surface area of BCl₃ layer are denoted by l and A , respectively. It is supposed that Xe molecules which come out of the BCl₃-Xe layer diffuse only in the x direction through the BCl₃ layer. Thus, Fick's second law of diffusion^{5,6)} gives

$$\partial c / \partial t = D(\partial^2 c / \partial x^2), \quad (1)$$

where c is the molar concentration of Xe, and D is the diffusivity of Xe in the BCl₃ layer. Solving Eq. (1) for the steady state with a constant evacuation speed S , and the boundary conditions that

$$\text{at } x=0, \quad c=c_0 \quad (2)$$

$$\text{at } x=l, \quad -D(dc/dx) = (S/A)c_l, \quad (3)$$

we get the concentration ratio of the value at $x=l$ to that at $x=0$ as

$$c_l/c_0 = AD/(AD + Sl) \equiv \alpha. \quad (4)$$

Suppose that the diffusivity will change from D to D^* under laser irradiation. Relating to this change, the Xe concentration at the surface will become c_l^* . Therefore, the ratio the diffusivity under irradiation to the original value is given by

$$D^*/D = (1-\alpha)\beta/(1-\alpha\beta), \quad (5)$$

where

$$\beta \equiv c_l^*/c_l. \quad (6)$$

The sublimation rate of Xe is defined by the molar flux of Xe at the surface, that is Sc_l^*/A or Sc_l/A according as the sample is irradiated or not. The surface area A and the evacuation speed S are independent of laser irradiation, and hence the ratio of sublimation rate under irradiation to that without irradiation is equal to β . The change of the ratio D^*/D with β is plotted in Fig. 2, with α as a parameter.

Next, we show in terms of probabilities that a small increase in molecular size of a solid will give a large decrease in gas diffusivity in the solid. Molecules of Xe would diffuse in the BCl_3 layer in complicated zigzag motion. In order to treat this motion mathematically, we simplify the pattern of the molecular motion. That is, gas molecules are considered to move in six directions: $\pm x$, $\pm y$, $\pm z$, and the distance a of translation by one jump is the same in all directions. Therefore, molecules move along the channels which connect the sites of primitive cubic lattice.

Fig. 2 The relation between the ratio of diffusivities D^*/D and the ratio of sublimation rates $c_l^*/c_l \equiv \beta$, with the concentration ratio $c_l/c_0 \equiv \alpha$ as a parameter.

Now we calculate the probability Q that Xe molecules will jump in any positive or negative x direction by one trial. Let p denote the probability that a passage in one direction is blocked and $(1-p)$ the probability that the passage is possible. The probability that r channels are open among n channels is given by $\binom{n}{r} (1-p)^r p^{n-r}$. If we take $+x$ channel is open, n becomes 5. The probability that the $+x$ channel is hit by one trial among open channels is $1/(r+1)$. There are six cases depending on from $r=0$ to 5, and the transitions through the $+x$ channel and through the $-x$ channel are independent and exclusive each other. Then, the probability that one Xe molecule can travel in any positive or negative x direction by one trial is

$$Q = 2 \sum_{r=0}^5 \binom{5}{r} (1-p)^{r+1} p^{5-r} / (r+1). \quad (7)$$

If we write $Q(p=0) = Q_0$, $Q_0 = 1/3$. The normalized probability Q/Q_0 is plotted against p in Fig. 3. "A trial" in terms of probabilities

Fig. 3 The normalized probability of Xe translation Q/Q_0 against the probability of blocking a passage, p . The solid line is obtained by the analytical solution, and the points by a Monte Carlo simulation.

corresponds physically to "a collision" by a Xe molecule against the plane perpendicular to the path concerned. Then, if Z is the number of collisions by one Xe molecule against the plane per unit time, the diffusivity of gas in solid is given by⁶⁾

$$D = QZa^2 = Qva, \quad (8)$$

where v is the translational velocity of the gas molecule around a site. It may be noted in this connection that the magnitude of D is $\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the probable values of $Q=0.1$, $Z=10^{12} \text{ s}^{-1}$ and $a=10^{-8} \text{ cm}$.

A Monte Carlo simulation has also been performed, by using the same simplified zigzag pattern as in the analytical treatment. The average number of jumps $\bar{N}$ needed for one Xe molecule to pass through a given number of layers n is calculated, under the condition that the incident molecules at the inner boundary are not allowed to move backward. In Fig. 4 (a), the number $\bar{N}$ obtained by random sampling is plotted against the number n with the probability p as a parameter. The value $n^2/\bar{N}$ is a Monte Carlo estimate of Q . One can easily see from Fig. 3 that $\bar{N}_0/\bar{N}$ agrees well with Q/Q_0 for various of p , where $\bar{N}_0$ stands for $\bar{N}$ at $p=0$. The value $n^2/\bar{N}_0 (=1/3, \text{ in an infinite cubic lattice})^{7)}$ is also plotted against n in Fig. 4 (b). It is seen that 50 layers of solid molecules are such as to make the boundary effect negligible in the diffusion. And in our solid samples, several tens of BCl_3 molecular layers were considered to form at the surface.

3. Discussion and Conclusion

In our experiments, the evacuation speed S is measured to be $3 \times 10^3 \text{ cm}^3 \text{ s}^{-1}$, and the surface area A of a sample is 3 cm^2 . On the other hand, probable values are: $D=10^{-5}$ (in liquid) $\sim 10^{-11}$

Fig. 4 The average number of jumps $\bar{N}$ by a Monte Carlo simulation for Xe to go through BCl_3 layers against the number of the layers n for many samplings, where the sampling size is 250 for $n=50$ and 1000 for other cases (a), and the value of $n^2/\bar{N}_0$ against n (b).

(in solid) and $l=1 \sim 10 \times 10^{-4} \text{ cm}$. Therefore, α is always close to zero, and Eq. (5) becomes $D^*/D = c_l^*/c_l$. Thus, the decrease in diffusivity by laser irradiation is closely related to the decrease of the sublimation rate.

For the interaction between Xe and BCl_3 , it is supposed that the probability of inhibiting Xe transfer between sites will increase by the increase in the cross section of BCl_3 molecules perpendicular to the Xe path. According to infrared spectroscopy⁸⁾, the increase in amplitude by vibrational excitation is estimated for the BCl_3 ν_3 frequency. The length of B-Cl bond changes by $\pm 3.7\%$ around the value ($\nu=0$) by excitation ($\nu=1$). During the period of Xe translation between sites, a molecule of BCl_3 vibrates

several tens of times in the excited ν_3 mode. Therefore, the increase in the amplitude of the BCl_3 vibration will have an effect of increasing the apparent molecular size of BCl_3 . Depending on a planar BCl_3 molecule being parallel or perpendicular to the axis of Xe translation, the change in molecular size will have an effect on the probability p by a linear or a square dependence. Supposing the random orientation of BCl_3 molecules with the predetermined size of atoms, the increase in the probability p by vibrational excitation may be estimated as $\sim 3\%$. It is seen from Fig. 3 and Eq. (8) that a few percent increase of p can decrease D by a large fraction, if $p \geq 0.9$. The one-to-one correspondence is found from Fig. 2 between the decrease of c_l and the decrease of D , in our experiments. Thus, it may be concluded that the decrease of Xe sublimation rate by laser irradiation is caused by the decrease of Xe diffusivity in the BCl_3 layer, through the small increase of apparent molecular size of BCl_3 by vibrational excitation.

It may be preferable that the estimation of the effect of BCl_3 molecular vibration on the probability p could be made with more precise treatment such as Molecular Dynamics Method. This problem is left in future, however, even with above described simplified model of

diffusion, the phenomenon that laser induced suppression of sublimation can be elucidated by the proposed mechanism.

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