Electronic Excitation Induced Desorption of Excited Atoms and Excimers from the Surface of Solid Ne

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Abstract

Desorption of an excited dimer Ne 2^* in 3_u state from a surface of solid Ne initiated by the creation of a valence exciton was confirmed experimentally for the first time using a low energy electron and a monochromatic VUV light as excitation sources. The kinetic energy of a desorbed excimer (Ne 2^*3 u) was (0.2 ± 0.1) eV, which is consistent with a recent quantum mechanical calculation. It is found that the vibrational relaxation of the molecular type exciton is slow process compared to the time scale of desorption. Desorption of excimers at the excitation of the first order surface exciton was found to be inefficient compared to that by the creation of bulk excitons, which is in striking contrast to the case of the excited atom desorption. The mechanism of excimer desorption can be explained by the cavity ejection model as in the atomic desorption case.

INTRODUCTION

Desorption of excited particles from the surface of rare gas solids has been extensively studied in these 10 years[1]. Monochromatic synchrotron radiation has made it possible to study detailed electronic excitation processes which lead to the desorption (table 1). As to the desorption of excited atoms induced by exciton creation, two desorption mechanisms (fig. 1), cavity ejection (CE) and excimer dissociation (ED), have been proposed[2] and the experimental results have been successfully explained by these models[3] (figs. 4 and 5).

Exciton initiated desorption of an excimer has been predicted theoretically for Ne, Ar and Kr solids, while experimental evidence has been obtained only for Ar [4]. In our previous work [5], we have observed the emission from the desorbed particles with long life-time from the surface of solid Ne, which is thought to be closely related to Ne2* desorption. Here we present the results of systematic measurements of the desorption of excited dimers from the surface of solid Ne initiated by an exciton creation using a low energy electron and a monochromatic VUV light as excitation sources.

Two kinds of experiments, electron stimulated desorption (ESD) and photon stimulated desorption (PSD), have been performed using a similar experimental setup (figs. 2 and 3). We have measured the spatial distribution of the VUV light emitted from the desorbed particles (fig. 6) and confirmed the desorption of Ne2*. From the results of lifetime measurements of the desorbed excimer, we have obtained the information on the vibrational states of desorbed excimer (figs. 7-10). Mechanism for the excimer desorption will be discussed from the present results.

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Table 1

Kinetic Energies and Electronic States of Desorbed Ne*

	Electronic Configuration	Excitation Energy	Kinetic Energy (eV)	Mechanism	Electronic State at Desorption (<i>tentative</i>)
S1	2p ⁵ 3s	17.2 eV (72.3 nm)	0.18	CE	2p ⁵ 3s (³ P _{0,2})
B1	2p ⁵ 3s	17.5 eV (70.7nm)	0.18	CE	2p ⁵ 3s (³ P _{0,2})
S'	2p ⁵ 3p	19.0 eV (65.4nm)	0.19 0.2 ~ 0.4 1.5	CE (bulk?) CE ED	2p ⁵ 3p 2p ⁵ 3p
B2	2p54s	20.3 eV (61.1nm)	0.18 0.36 1.5	CE CE (?) ED	$2p^{5}3s (^{3}P_{0,2})$ $2p^{5}4s (?)$
B3	2p55s	20.9 eV (59.2nm)	0.18 0.36 1.5	CE CE(?) ED	$2p^{5}3s (^{3}P_{0,2}) 2p^{5}5s(?)$



Schematic Diagram of the Experimental Apparatus (Top View)









Apparent peak appeared around $t_d = 5 \ \mu s$ is attributed to the superposition of an exponential decay curve, which starts at $t_d = 0 \ \mu s$, and a dip at $t_d \sim 2 \ \mu s$. The dip is due to the delay corresponding to the time t_e which is needed for the desorbed excited particles to escape from the '*shadow*' region made by the edge of the heat shield.

Figure 4

Desorption of Excited Atoms from Solid Ne [PSD]



All figures are adopted from ref.[6].

Angular Distribution of Desorbed Ne*(CE) [PSD]



Angular distribution of Ne^{*} desorbed from the surface of solid Ne by the creation of S1, B1 and S' excitons via cavity ejection mechanism [7]. Red circles are the measured points, and blue lines are the fitting curves using $\cos^n \theta$. Results for ED component show much broader angular distribution $(0 \ n \ 1)$.

Two Dimentional Spatial Distribution of Emission Plume from the Surface of Solid Ne [ESD]



Two dimensional image of the spatial distribution of the emission from the excited particles desorbed from the surface of solid Ne measured at (a) θ =13 deg, (b) θ =15 deg, and (c) θ =17 deg. An arrow in (a) shows the incident electron beam. The sample is located at *X* =0. The direction of '*X*' and '*Y*' is designated in Fig.3. Note that the intensity is normalized to the maximum of the plume in each image.



Decay curves of the emission [ESD]



Decay curves for the emission measured at the angle of the cryostat θ of 13,15 and 17deg with an electron impact energy of 200eV. The inset shows the curve measured at $\theta = 15$ deg. in semi-logarithmic scale, indicating the non-single exponential type decay.



Dependence of the decay curve on the sample thickness measured at an electron impact energy of 200eV. The slower component appeares only at the thicker sample.

Decay curve measured at an electron energy below band gap energy of solid Ne [ESD]

Figure 9



Decay curve measured at an electron impact energy of 19.5 eV, which is well below the band gap energy of solid Ne (21.6eV), The curve also shows the non-single exponential type decay. Inset shows time-of-flight spectra of desorbed Ne* used for the calibration of the impact energy of electron.

Population of Vibrational Levels of Desorbed Ne₂*



Relative population P(v) for desorbed excimer measured with the sample thicknesses of 8, 30, 140, and 550 atomic monolayers (ML). Vibrationally relaxed excimer desorbs only from thick sample.

Dependence of Desorption Yield of Ne₂* on Excitation Wavelength [PSD]



Desorption yield of Ne₂^{*} (3 _u) as a function of the wavelength of incident light (a). Desorption yield of Ne^{*}(CE) [6] is also shown in (b) for reference.

Dependence of Emission Lifetime on Vibrational Levels

Observed non-single exponential decay curves

Vibrational Distribution of Desorbed Excimer

Schneider and Cohen [8] predicted a significant dependence of the lifetimes of Ne₂* $(^{3}$ u) on the vibrational level *v*. (See Table 2)

Multi-exponential fitting has been done for the exponential part of the decay curves (figs. 7&8) using an equation below.

$$I(t) = \int_{i=0}^{7} A_{v} \exp(-\frac{t}{B\tau_{v}})$$

$$A_{v}: \text{ pre-exponential factor}$$

$$\tau_{v}: \text{ emission lifetime of Ne}_{2}*(3 \text{ u}) \text{ by Schneider and Cohen [8]}$$

$$B: \text{ Correction factor for the results of Schneider and Cohen}$$

Population of the vibrational level of desorbed excimer was calculated using an equation below, and plotted in fig.10.

$$P(v) = {}_{0}A_{v}\exp(-\frac{t}{B\tau_{v}})dt = A_{v}B\tau_{v} \qquad \text{where} \qquad {}_{v=0}'P(v) = 1.$$

Table 2. Emission Lifetimes for Ne₂* (3 u)

V	0	1	2	3	4	5	6	7
τ_V (µs)	11.9	10.2	8.8	7.7	6.6	5.6	4.5	3.5
$\tau_{V'}$ (µs)	8.5	7.2	6.2	5.5	4.7	4.0	3.2	2.5

 τ_v : Emission lifetime of vibrational level *v* calculated by Schneider and Cohen [8] $\tau_{v'}$: Present results with a correction factor *B* = 0.71.

DISCUSSION

- Confirmation of the validity of Cavity Ejection (CE) and Excimer Dissociation (ED) mechanisms for an excited atom desorption (figs.1, 4 and 5).
- Preferential desorption of vibrationally unrelaxed excimer, i.e., desorption of an excimer before the vibrational relaxation (fig. 10). time scale: vibrational relaxation of a molecular exciton in solid Ne > 10^{-7} s desorption of an excimer < 10^{-11} s radiative lifetime of an excimer > 10^{-6} s
- Desorption of vibrationally relaxed excimer only from thick sample (figs.8 and 10). Thickness dependence (fig.8) of the decay curve suggests the surface-like and bulk-like feature for the vibrationally unrelaxed and relaxed excimer desorption, respectively. There is no clear explanation for this results where and how the vibrational relaxation occurs at present.

possible interpretation

▲ If the dissociation of an excimer in the bulk occurs, an energetic atom in excited state is created. It can migrate (move) toward the surface, and dimerize with a ground state atom near the surface, and desorbs as an

- excimer. Effective vibrational relaxation can be expected to occur during the dimerization.
- ▲ Molecular dynamics calculation for solid Ar shows ineffective desorption of vibrationally relaxed Ar₂* from damaged (rough) surface[9]. For the preparation of a thin sample we expose the sample to Ne gas of rather low pressure (~10⁻⁶Pa), while higher pressure (10⁻⁴Pa) is used for thicker sample, where the sample surface may be annealed due to the heat of condensation.
- Estimation of kinetic energy of the desorbed excimer (fig. 7). Kinetic energy of the desorbed excimer was estimated at (0.2 ± 0.1) eV from a geometrical condition and the position of the apparent peak in fig.7. Chen et al. [10] calculated the kinetic energy of Ne₂* to be 0.23eV using an extended ion method, which is in good agreement with the present results.
- Inefficient desorption of an excimer by the creation of the 1st order surface exciton (S1) compared to the atomic desorption case (fig.11).

An excited atom on the surface can desorb in 10^{-12} s, which results in the decrease of the efficiency of the excimer formation on the surface.

ESD results show the efficient desorption of an excimer from the surface (fig.8).

difference of the penetration depth of electron and photon into the solid Ne

- hv 3nm (~ 11 ML)
- e 1nm (~ 3 ML) higher sensitivity for surface
- Relative desorption yield at S' exciton remains almost the same compared to that of bulk exciton.
 A sequence of an exciton by S' exciton (2n52n) consistent with the

efficient formation of an excimer by S' exciton (2p⁵3p), consistent with the observation of luminescence from molecular-type luminescence by Inoue et al. [11]

• Desorption mechanism for Ne₂* Cavity Ejection Mechanism.

Validity of cavity ejection mechanism is supported by following results;

- low kinetic energy of desorbed excimer
- the same order of magnitude of the kinetic energy as atomic desorption case
- desorption of an excimer at an excitation energy lower than band gap energy, even at S1 excitation
- agreement with a theoretical calculation [10], which supported CE mechanism for the excimer desorption.

SUMMARY

We have performed the photon- and electron-stimulated desorption experiments from the surface of solid Ne using low energy electrons and photons, and have confirmed the desorption of a Ne excimer in 3 u state from the surface by a creation of valence exciton. We should emphasize that the present work is the first systematic report on the excimer desorption from the surface of solid rare gas purely induced by valence exciton creation.

It is found that most of the desorbed excimer is in highest vibrational level indicating the very fast desorption process compared to the vibrational relaxation. Desorption of vibrationally relaxed excimer has been observed only with a thick sample, suggesting an efficient vibrational relaxation of the excimer created in the bulk, although at present we have no definite idea to explain where and how the relaxation occurs. Kinetic energy of the desorbed excimer is found to be 0.2 ± 0.1 eV, which suggests that the excimer desorption occurs via a cavity ejection mechanism as in the excited atom desorption.

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