多価イオンと希ガス固体表面の相互作用

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1　はじめに

希ガス固体表面あるいは固体中に励起原子（励起子）を生成すると，様々な緩和過程の後に粒子の脱離が観測される。この現象は電子遷移誘起脱離 (DIET: Desorption Induced by Electronic Transitions) と呼ばれ，固体表面上での動的過程に関連した現象として注目され，1980 年頃から盛んに研究されている。我々は以前から希ガス固体表面を標的として，低エネルギー（$\leq$ 100 eV ）電子あるいは真空紫外光入射により脱離する準安定励起原子および基底状態原子を観測することにより，励起子緩和の動的過程に関する様々な知見を得ている。

固体表面と低エネルギー多価イオンの相互作用に関する実験的研究は，近年の多価イオン源の発展に伴いさまざまな系に対して行われている。しかし，それらのほとんどの報告例は標的固体が金属・半導体であり，絶縁物を標的とした場合はその実験的困難さから標的の系が非常に限られている。

本研究では希ガス固体を標的として，巨大な内部エネルギーを持つ低エネルギー多価イオンビームを照射し，固体表面および固体中での劇的な構造変化を伴うさまざまな緩和過程を，主に脱離粒子の測定により観測し，Van der Waals 力により結合している非常にもろい希ガス固体の表面および固体中で，多価イオンの持つ巨大な静電エネルギーがどのように消費されるのかを定量的に明らかにすることを目的とした実験を行っている。また，希ガス固体中での電子的励起の素過程に関する情報を得るために，低エネルギー（$\leq$ 100 eV ）電子ビーム衝撃による実験も並行して行っている。

2003 年度は以下の研究を行った。

- 低エネルギー電子衝突により固体 Ne 表面から脱離する準安定励起原子の脱離角度分布の測定。
- 多価イオンビーム衝撃による希ガス固体からの絶対脱離収率の測定。
- 多価イオンビーム入射により希ガス固体表面で反射したイオンの価数分布の測定。
- 多価イオンビーム入射による希ガス固体表面からの脱離イオンと反射イオンの同時計測。

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2　実験装置

本事業により製作した実験装置の全体図を図 1 に示す。Electron Cyclotron Resonance (ECR) 型多価イオン源（マイクロ波周波数：10GHz，マイクロ波出力：100W），NANOGAN (Pantechnik 社製) により生成した多価イオンビームを 10 – 20 kV の引き出し電圧で引きだし，質量選別器で必要な価数のイオンを選び，収束レンズ系および減速レンズ系を通して衝突チェンバーに導いている。多価イオンの衝突エネルギーは 0.1 - 2 $q$keV (q: イオンの価数) である。

希ガス固体のような低温凝縮表面を標的とした場合，1×10^{-8} Pa 以下の極高真空下で実験を行うことが必要であるが，多価イオンビームラインにおける圧力は 5×10^{-6} Pa 程度であるため，差動排気系を設置した。これにより，実験中の衝突チェンバーの圧力を 1×10^{-8} Pa 程度に保つことが可能となった。

衝突チェンバーはタンデム式ターボ分子ポンプと Ti ゲッターポンプにより排気され，摂氏 150 度 24 時間の焼きだし処理後，5×10^{-9} Pa の到達圧力を得ている。希ガス固体試料は機械式冷凍機で 4.3 K 程度まで冷却された多結晶銅基盤上に生成した。本実験で用いた希ガス固体試料の膜厚は 200 $\sim$ 400 原子層程度である。2003 年度には，真空槽中心を軸として試料を回転するための機構を新たに導入した。これにより超高真空を保ったまま試料を任意の角度に回転させることが可能となった。また，全脱

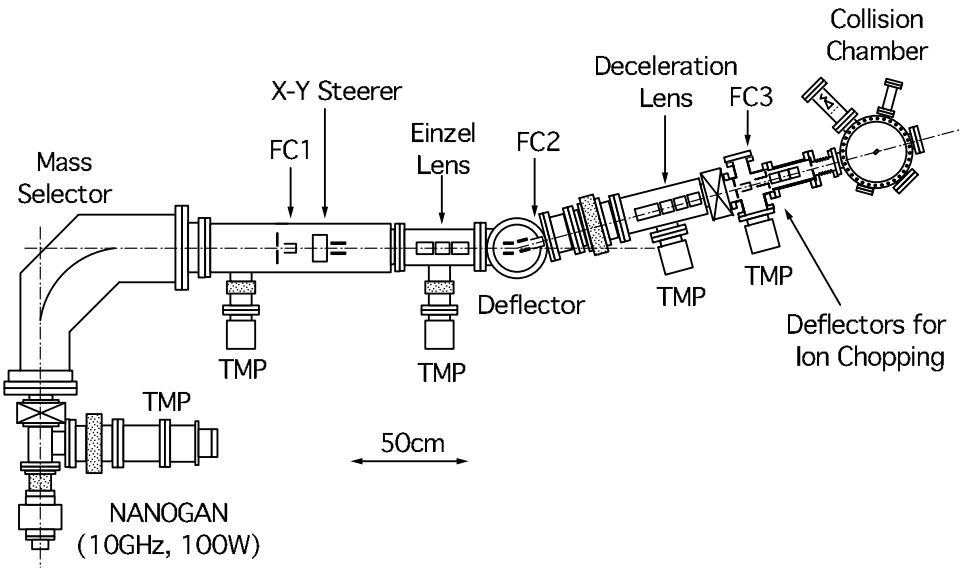

図 1: 実験装置全体図

離収率測定用に四重極型質量分析計を設置した。電子衝撃実験による脱離角度分布を測定するため新たに電子銃を設計・製作した。電子銃は機械式の冷凍機の熱シールド部に固定されていて，試料と同時に回転が可能である。パルス化（パルス幅：約 $1\mu s$）した電子ビームを希ガス固体表面に入射し，脱離したイオンおよび準安定励起状態の原子を真空槽に固定したチャンネル型二次電子増倍管で検出した。

多価イオンビームは差動排気室にある偏向板によりパルス化した。パルス幅は 0.5 – 1 μs 程度，パルス周波数は 1 – 10 kHz である。試料基板に正のバイアス電圧を印加することにより，希ガス固体表面から脱離したイオンを加速し，二次電子増倍管で検出した。また，イオンの反射位置に新たに反射イオン測定用検出器を設置した。

3　電子衝撃による励起原子の脱離

2003 年度は，試料温度可変のクライオスタットを用いて，低エネルギー電子衝撃による固体 Ne からの脱離励起原子の脱離角度分布を測定した。Cavity Ejection 機構により脱離する励起原子は表面垂直方向に優先的に脱離することが知られている。4.3K で生成した Ne 固体を標的とした場合と 7K でアニールした試料を用いた場合では，その角度分布を $\cos^n\theta$ で Fitting したときの n が 14 から 19 に増大し，アニールをすることにより角度分布がより鋭くなることが分かった。これはアニールにより試料が結晶化し対称性の高い表面となった結果であると説明できる。

4　多価イオン・固体Ｎｅ衝突実験

2001 年度にハイテクリサーチセンター整備事業により購入した電子サイクロトロン共鳴 (ECR) 型多価イオン源を使用して，多価イオン・希ガス固体相互作用に関する実験を行っている。

2003 年度は新たに反射イオン測定用の検出器を製作し，反射イオン・脱離イオンの同時計測を目的としたシステムを構築し，その動作確認を行った。反射イオンの価数分布を測定することにより，固体を構成する原子から多価イオンに移動した電荷数を特定することが可能となり，希ガス固体表面から脱離するイオンの脱力行に関するより詳細な情報が得られることが期待される。予備実験において同時計測信号を得ることができたが信号強度が十分ではなく，現在，より感度の高い計測ができるよう調整中である。

また，$Ar^{q+}(q:2\sim5)$ 入射による固体 Ne からの絶対脱離収率の測定を開始した。予備的実験結果

によると，入射多価イオン 1 個あたり 100 個以上の Ne 原子の脱離が確認された。現在，入射エネルギー・入射イオンの価数・試料膜厚依存性など，系統的な測定を行っている。

業績リスト（2001〜2003 年度）

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Absolute measurements of the total PSD and ESD yields at the surface of solid krypton

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Abstract

Absolute total desorption yields from the surface of solid krypton were measured by photo excitation at excitonic excitation energies and by electron excitation in the energy range between 70 and 320 eV. The absolute desorption yields and their dependence on the film thickness and on the excitation energy were quantitatively reproduced by a simulation based on the desorption model of excimer dissociation followed by internal sputtering.

Keywords: Desorption induced by electronic transitions (DIET); Electron stimulated desorption (ESD); Photon stimulated desorption (PSD); Noble gases

1. Introduction

Photon or electron irradiation of a surface of rare gas solids produces electronic excitations which can be followed by the desorption of various kinds of particles. Measurements of the initial excitation energy dependence of the desorption yields, by photo desorption experiments [1,2] typically, have provided important information on the initial stages of the desorption mechanism. Investigations of excited states, kinetic energy distributions, and angular distributions of desorbed species [3,4], have revealed the dynamics of the electronic excitation and relaxation in rare gas solids. The next step of the investigation is the determination of the absolute desorption yield [4,5], which will make clear the quantitative aspects of the process, for example, the branching ratios of relaxation channels.

We have reported the absolute yields of the metastable species [4] and the total desorption [5] from the surface of solid neon at the excitonic excitation by photo irradiation. The total desorption yield of about 0.1 Ne/photon at the excitation of the surface exciton was quantitatively explained by the cavity ejection (CE) mechanism in which the desorption probability of the surface exciton was almost unity. The higher yield caused by the bulk exciton excitation was also quantitatively explained by CE from the second or third underlying layer accompanied by internal sputtering [5]. In the case of Kr, the majority of desorbed species is thought to be ground state neutrals originated

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by the dissociation of an excited dimer (excimer) in the solid. The kinetic energy of about 0.8 eV that is released by the excimer dissociation (ED) is imparted to the two Kr atoms and propagated via collision cascade between neighboring atoms and may lead internal sputtering if the ED occurs in the vicinity of the surface. The kinetic energy distribution of the desorbed ground state Kr atoms, which was measured by a time of flight (TOF) technique using keV electron and He ion beams as an excitation source [6], was successfully reproduced by the classical molecular dynamics (MD) calculation by Dutkiewicz et al. [7] on the assumption of ED, a collision cascade, and internal sputtering. In the MD calculation, the average number of atoms sputtered was calculated for a given depth where the ED occurred. The film thickness dependence of the desorption yields, which was measured for keV light ion bombardment [8], indicates that long range energy transfer occurs and that the electronic excitation energy embedded in the bulk can contribute the desorption.

In the present study, we report the results of the absolute measurements of the total desorption yields from the surface of solid Kr by photo excitation and by electron excitation. We also show that the "absolute" values of the desorption yields are well explained by the simple model calculation of desorption process.

2. Experimental

The electron stimulated desorption (ESD) experiment was carried out in Gakushuin University and the photon stimulated desorption (PSD) one at beamline BL5B in UVSOR facility, the Institute for Molecular Science, Okazaki, Japan. The details of these experimental apparatuses have been described elsewhere; ESD [9] and PSD [9,10]. For both experiments, a liquid helium cryostat, a quadrupole mass spectrometer, and an ionization gauge were installed in a main vacuum chamber with a base pressure less than 1×10^{-8} Pa, which is equipped with a gas handling system. The absolute total desorption yield was calculated from the partial pressure rise of desorbed species during the photon or electron irradiation, the absolute flux of the incident photon or electron beam, and the pumping speed of a turbo molecular pump and the cold surface of the cryostat for the desorbed species. The quadrupole mass spectrometer for the partial pressure measurement was calibrated by the ionization gauge at each run of the measurement. The pumping speed was determined from the pressure which was measured by the ionization gauge in the main chamber and from the flow rate which was measured volumetrically using a reference volume and a Baratron pressure gauge of the gas handling system. In the PSD experiment, the photon flux was simultaneously monitored by measuring a photoelectron current emitted from the gold plated mesh which was inserted in the beam line. The quantum efficiency of photoelectron emission of gold was adopted from the data reported by Cairns and Samson [11]. The fraction of the higher order light from the monochromator reached about 40–60% of the total photon flux in the wavelength range between 80 and 130 nm [12], for which suitable compensation was made in the calculation of the absolute yield. The film of solid rare gas was prepared by condensing gas on the cold surface of a platinum (PSD) or a copper substrate (ESD) attached to the liquid helium cryostat. The sample temperature was about 6 K. The film thickness was calculated from the exposure, the product of pressure and exposing time of gas, on the assumption that the condensation coefficient of Kr was unity.

The uncertainty in determining the absolute desorption yield is estimated at as large as $\pm 1/3$ of the order of magnitude; error bars ranging from a half to twice the measured value should be added in the figures. It was mainly caused by the uncertainty in the pressure measurement and, in the case of PSD experiment, in the intensity estimation of the incident photon flux. Noticeable changes in the desorption yields were observed after a few hours exposure of the sample in the chamber at a pressure of lower 10^{-8} Pa range. It was probably due to adsorption of the common residual gases in a UHV system; H_2, H_2O, CO, etc. The uncertainty caused by this impurity effect is within the error bar above mentioned.

3. Absolute desorption yields and its thickness dependence

3.1. PSD measurement

The wavelength dependence of the photo-desorption intensities from the solid Kr for three different film thickness is shown in Fig. 1, where the curves are the direct output from the mass spectrometer with no compensation applied for the higher order light. The arrows show the wavelength corresponding to the excitation of the series of excitons in solid Kr. The coincidence between the exciton excitation energies and the peaks or shoulders in the figure clearly shows that the excitons play an important role in the desorption process. The desorption yields which were directly due to excitonic excitations were estimated by the peak height above the continuous background which was due to the bulk ionization caused by the higher order light from the monochromator. The absolute desorption yields by the excitations of S1(3/2), B1(3/2), and B1(1/2) excitons are shown in Fig. 2 as a function of the film thickness. The desorption yield at S1(3/2) excitation has apparently no thickness dependence and is about 0.015 atoms/photon. The desorption by the bulk exciton creation becomes detectable at a few tens atomic layers in our experimental condition. The desorption yields at B1(3/2) and B1(1/2) excitation increase with the film thickness and reach a value of saturation at the thickness of about 100 atomic layers, 0.03 and 0.02 atoms/photon, respectively.

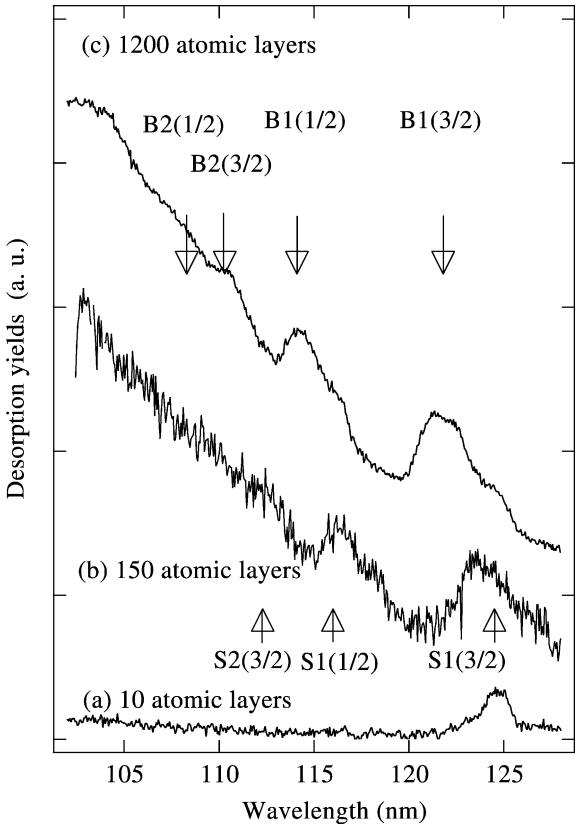

Fig. 1. Wavelength dependence of total photo-desorption yield from solid Kr. The film thickness is (a) 10, (b) 150 and (c) 1200 atomic layers. The abbreviations for the exciton states are as follows; B: bulk, S: surface, number: order, 1/2 and 3/2: the total angular momentum of the p-hole.

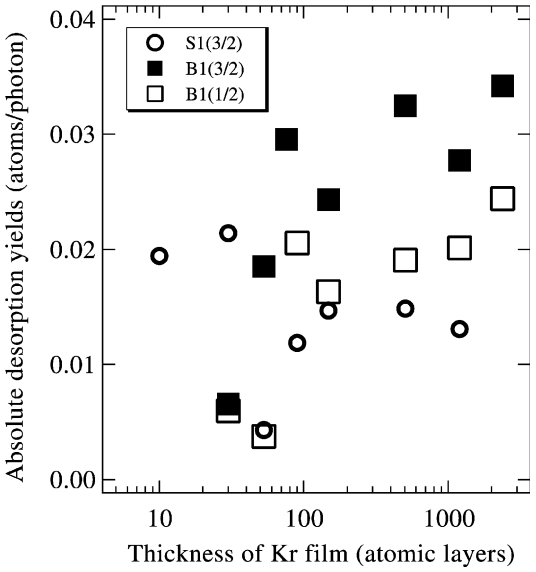

Fig. 2. Thickness dependence of the PSD yields of krypton by bulk and surface excitonic excitation.

3.2. ESD measurement

The absolute ESD yields and the thickness dependence at the incident electron energy of 220 eV are shown in Fig. 3. The yield increases with film thickness and seems to be saturated above 100 atomic layers.

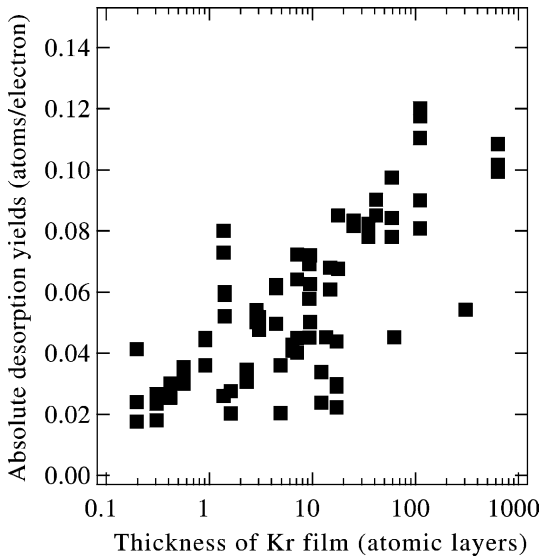

Fig. 3. Thickness dependence of the ESD yields of krypton at the excitation energy of 220 eV.

4. Desorption model and simulation of desorption yields

The desorption process caused by ED and internal sputtering can be considered as six sequential steps: (i-1) creation of free excitons or (i-2) creation of electron–hole pairs (ionic state), (ii) migration of these excited states, (iii) formation and (iv) dissociation of excimers, (v) kinetic energy transfer by collision cascade, and (vi) internal sputtering near the vacuum interface. To estimate the final desorption yields, each step is examined and quantitatively evaluated.

(i-1) Creation of excitons: Under the condition of selective excitation by a monochromatic light in PSD experiment, the density distribution of the excitons created in the bulk is estimated from the absorption coefficient μ of light. The number of excitons $I(x)\mathrm{d}x$ created between x and $x + \mathrm{d}x$ of the distance from the vacuum interface is

$$I(x)\,\mathrm{d}x = I_0\mu \mathrm{e}^{-\mu x}\,\mathrm{d}x, \tag{1}$$

where I_0 is the initial photon flux. The absorption coefficient μ of Kr at B1(3/2) excitation energy is 1.5×10^6 cm^{-1} [13].

(i-2) Ionization in bulk: An electron beam with energy much higher than the ionization energy can produce a number of electron–hole pairs on its track in solid Kr. The distribution of the electron–hole pairs was calculated on the assumption that the incident electron loses a mean energy W at each ionization [14] on the straight track which is normal to the surface of the film. In order to estimate the mean free path of the electron in Kr film, we used the data of the ionization cross section and its energy dependence of an isolated atom, namely in the gas phase. Fig. 4 shows the result of the simulation for the incident energy of 220 eV.

(ii)–(iii) Migration of the excited states and the formation of excimers: The created free excitons or ionic states can diffuse in the solid. The density distribution of the mobile excited state $n(x)$ in the steady state can be modeled by the following equation,

$$D\frac{\mathrm{d}^2 n(x)}{\mathrm{d}x^2} - \frac{n(x)}{\tau} + I(x) = 0, \tag{2}$$

where D is the diffusion coefficient of the mobile excited state, τ is the lifetime of the mobile state, and $I(x)$ is the initial distribution described in (i-1) or (i-2). We assumed here a single τ to characterize trapping of the mobile state into the molecular type self trapped exciton because, in the case of heavier rare gas solid (Kr and Xe), most of the excitonic excitation forms an excimer. It has been

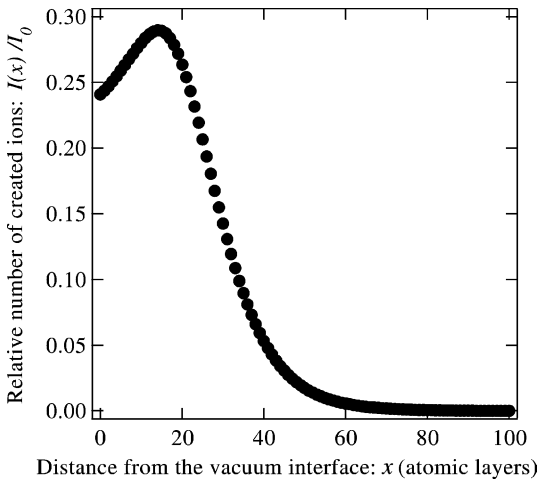

Fig. 4. Calculated distribution of the number of ions created in the film by 220 eV electron bombardment.

revealed in a photoemission study [15] that the branching ration of the decay from an atomic type exciton into the ground state is much smaller than that into excimer formation in solid Kr and Xe. The behavior of the excited states at the interfaces with vacuum and with the metal substrate determines the boundary conditions on Eq. (2). Though the dynamics of excitons at these interfaces are not well understood, the photoemission data of Kr were best described by assuming that the metal surface is a perfect sink and the vacuum interface is perfect reflector for the exciton [16]. The experimental results of MeV light ion bombardment on a solid argon film are also consistent with the metal surface being a perfect sink [17]. For both the exciton and the ionic state, we assumed two boundary conditions as follows,

$$\frac{dn(0)}{dx} = 0, \tag{3}$$

$$n(d) = 0, \tag{4}$$

where d is the thickness of the sample film. Eqs. (3) and (4) correspond to the vacuum interface being a perfect reflector and the metal substrate being a perfect sink, respectively. Eq. (2) is transformed into the following equation,

$$L^2 \frac{d^2N(x)}{dx^2} - N(x) + I(x) = 0, \tag{5}$$

$$L^2 = D\tau, \tag{6}$$

$$N(x) = \frac{n(x)}{\tau}, \tag{7}$$

where L is the diffusion length of the mobile exciton or the ionic state and $N(x)$ is the rate of trapping into the excimer. Under steady state conditions, because all the excimers dissociate sooner or later, $N(x)dx$ is the rate of the dissociation, namely the release of kinetic energy, between x and $x + dx$. For given $I(x)$, Eq. (5) with boundary conditions (3) and (4) can be solved analytically or numerically with L as the only uncertain parameter. Fig. 5 shows the solution for the diffusion length L of 10 nm for four different film thicknesses in the case of B1(3/2) excitation by photon. The density of the excimers trapped in the vicinity of the vacuum interface, which contribute to the desorption, increases with the film thickness and reaches a saturated value. The pronounced effect of the diffusion length L on the magnitude of $n(0)/\tau$ is shown in Fig. 6 for the film of 1000 nm in thickness.

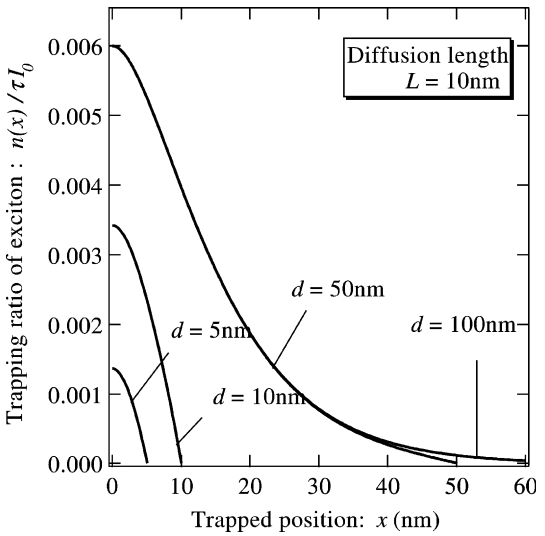

Fig. 5. Solution to Eq. (5) for the diffusion length $L = 10$ nm and for four different film thicknesses ($d = 5$, 10, 50, 100 nm).

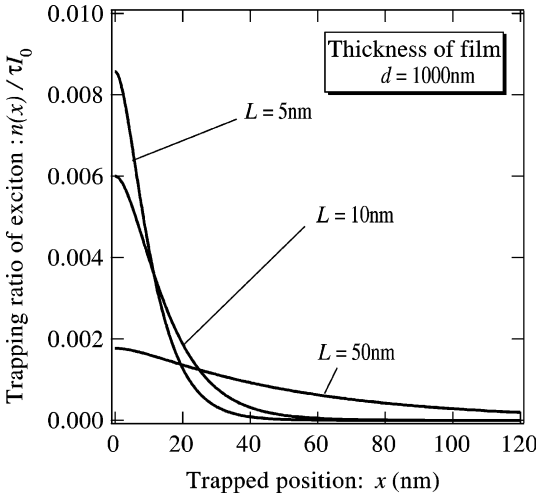

Fig. 6. Solution to Eq. (5) for various diffusion lengths L and for the film thickness d of 1000 nm.

(iv)–(vi) ED, collision cascade, and sputtering: The results of a classical MD calculation by

Dutkiewicz et al. [7] were adapted for use with the above results to estimate the desorption yields. In their calculation the number of ejected atoms was calculated as a function of the depth x where the release of kinetic energy occurred. The results of PSD simulation are shown in Fig. 7 with the experimental results for comparison. The curve calculated for the diffusion length L of 10 nm reproduces well both the thickness dependence and the absolute value of the desorption yield at saturation. The simulations of the thickness and the incident energy dependence for ESD are shown in Figs. 8 and 9, respectively. In the case of ESD, the saturated value of the yield and the incident electron energy dependence are well reproduced by the simulation with L of 30 nm while there is obvious discrepancy in thickness dependence for thin films.

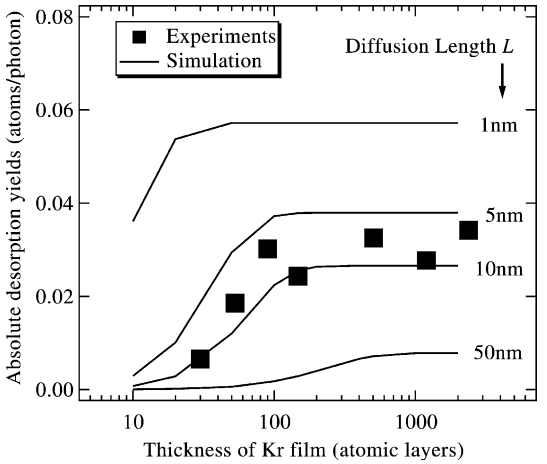

Fig. 7. Results of the model simulation of PSD yields by B1(3/2) excitation for different diffusion lengths ($L = 1$, 5, 10, 50 nm). The experimental results are shown for comparison.

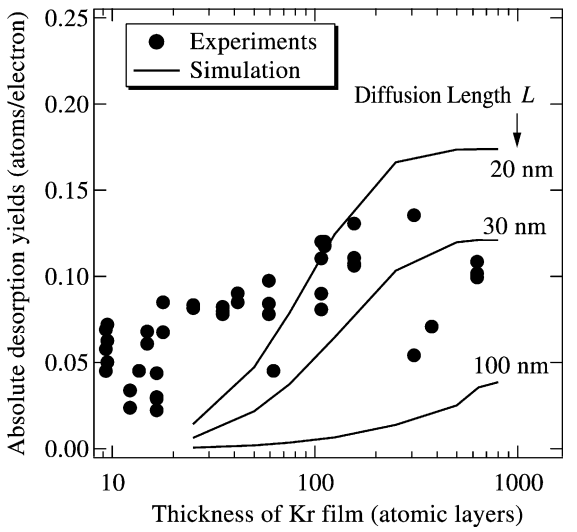

Fig. 8. Results of model simulation of ESD yields by 220 eV electron irradiation for three different diffusion lengths ($L = 20$, 30, 100 nm). The experimental results are shown for comparison.

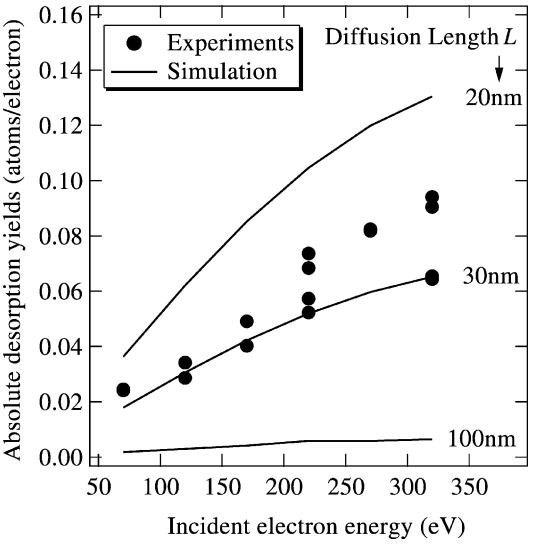

Fig. 9. ESD yields of incident electron energy dependence. Results of model simulation are indicated by solid line for three different diffusion length ($L = 20$, 30, 100 nm) and the experimental results are indicated by solid circles. Thickness of krypton film was 100 atomic layers.

5. Discussion

The absolute yield, the film thickness dependence, and the incident energy dependence of the total desorption from the solid Kr film were consistently and satisfactorily reproduced by adjusting the diffusion length L as the single parameter for simulation. For the PSD result in which bulk excitons in the B1(3/2) state are selectively excited by monochromatic light, L is that of the free exciton. Considering that the magnitude of L may strongly

depend on the crystalline condition and the temperature of the film, to say nothing of the theoretical derivation, it is not easy to make a critical comparison with other experimental results. We, however, refer to the result of the photoemission study by Schwentner et al. [16]. They have reported the diffusion length of the exciton in solid Kr of the range between 1 and 10 nm which is consistent with our value used in the simulation. In the case of ESD, the mobile excited states are thought to be not only the single excitonic state but those in higher states as well as ionic states. The diffusion length should be, therefore, the weighted average of them. From the desorption experiment under similar conditions by light ion bombardment with keV energy, Schou have estimated that the average diffusion length of the mixed higher excited states in Kr was 30 nm [8], which also shows good agreement with our simulation results. The discrepancy between the measurement and the simulation for thin films less than 100 atomic layers in ESD of Kr is thought to be caused by secondary electrons from the metal substrate, which were not considered in the present simulation. It should also be considered that the Antoniewicz mechanism [18] may work efficiently for films of a few atomic layers or less.

6. Summary

We have measured the absolute total ESD and PSD yields from the surface of solid Kr. At the films thicker than 100 atomic layers, the absolute photo-desorption yields are about 0.03 and 0.02 atoms/photon at the excitation energy of B1(3/2) and B1(1/2), respectively. In the case of 220 eV electron impact, the desorption yields is about 0.1 atoms/electron at the film thicker than 100 atomic layers. The uncertainty of these value would be $\pm 1/3$ of the order of magnitude. The absolute desorption yields and its dependence on the film thickness and on the excitation energy was calculated by the simulation based on the desorption model of the ED followed by collision cascade and internal sputtering. They were quantitatively reproduced by adjusting the diffusion length of the mobile excited state as the only parameter for simulation.

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