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Time response of photon-stimulated desorption of excited-state sodium atoms from sodium halides

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The time response of excited-state sodium desorption from NaF and NaCl has been investigated with synchrotron-radiation pulses. The decay curve of the Na *D*-line intensity from a desorbed excited-state sodium atom is found to consist of a fast component in the ns range and a slow component between 178 ns and 3 ms. This successful observation of the time response of excited-state alkali desorption suggests there are two types of desorption mechanism, a slow one originating from the thermal instability of surface defects and a fast one due to the lattice instability induced by an electronic transition in the surface layer.

In recent years, photon-stimulated desorption (PSD) has aroused considerable interest, because of its close relation to basic surface science and also because of its applicability to microfabrication. There have been many reports on desorption from alkali halide surfaces.[1] However, while most of them are limited to ionized or ground-state species, several works are reported about PSD of excited-state species from alkali halides.[2–6] Tolk *et al.*[2] observed PSD of excited-state alkali atoms from LiF and NaCl, and proposed that the desorption is induced by secondary electronic processes. Bunton *et al.*[3,4] have measured the excitation-photon energy dependence of PSD of excited-state alkali atoms from LiF, NaCl, and KCl in the energy range corresponding to valence-band and core-level excitations. The present authors[5] have observed PSD of excited-state alkali atoms from NaCl under valence-band and core-level excitations. Both results indicate that valence-band excitation as well as core-level excitation cause the desorption of excited-state alkali atoms. The present authors[5] have also measured substance and photon-flux dependences of excited-state alkali desorption from sodium and potassium halides and reported a close correspondence of the desorption yield to defect and self-trapped exciton (STE) formations. Liu *et al.*[6] have reviewed progress in PSD and proposed surface exoergic reactions between alkali dimers and halogen atoms for excited-state alkali desorption. Details of the PSD mechanism of excited-state alkali atoms are, however, still open questions. The purpose of the present work is to improve our understanding of the PSD mechanism by measuring the time response of excited-state alkali desorption. The present report describes the time response of PSD of excited-state alkali atoms from alkali halides; we note a previous unsuccessful trial by Haglund *et al.*[7]

The PSD experiments were carried out at a plane-grating monochromator (PGM) beam line of UVSOR Facility, Institute for Molecular Science. Ultrapure single crystals, which were purchased from the Crystal Growth Laboratory of the University of Utah, were cleaved *in situ* with a knife edge. The base pressure in a sample-preparation chamber was about 9×10^{-8} Pa and that in a main chamber was about 2×10^{-8} Pa during the measurements.

The desorption of excited-state sodium atoms was detected by measuring the Na *D*-line fluorescence due to the decay of excited Na atoms. Time response of the Na *D*-line intensity was investigated with synchrotron radiation pulses under a single-bunch operation. A time-correlated single-photon-counting technique was used with a microchannel plate photomultiplier (HAMAMATSU R2809U-07) through a Jobin-Yvon grating monochromator HR-320. The full width at half maximum of the incident photon pulse including the response of the detector system was about 480 ps and the time interval between subsequent pulses was 178 ns; any component slower than the time interval shows up as pileup in the background. The time response of the Na *D*-line intensity was also measured in the range of 3–300 ms by using a mechanical chopper. All experiments were carried out at room temperature.

Figure 1 shows emission spectra of NaF and NaCl excited with zeroth-order light from PGM through a 1000-Å-thick aluminum filter, the spectral distribution of which extends from 15 to 73 eV. The spectra have been corrected for the spectral sensitivity of the detecting system by using a tungsten standard lamp. The spectra consist of a sharp line at about 2.10 eV and broad bands. The sharp line is assigned to the Na *D* line from the decay of a desorbed excited-state Na atom. The broad bands may be ascribed to the recombination luminescence originating from defects produced by irradiation and are not of interest in this study.

Figures 2 and 3 show decay curves of the 2.10-eV emission intensity in NaF and NaCl, respectively. Curves (*a*) show the raw decay curves observed at 2.10 eV, while curves (*b*) show the decay curves of the broad band at 2.10 eV, which have been estimated from the observed profile of the emission spectra and the decay curves observed at 2.06 and 2.14 eV. Curves (*c*) are time responses of excited-state Na desorption, which have been derived by subtracting curves (*b*) from curves (*a*). As seen in curves (*c*) of Figs. 2 and 3, the time response of PSD of excited-state Na atoms is composed of two components; that is, a fast component in the ns range and a slow component observed as background. We tried to determine

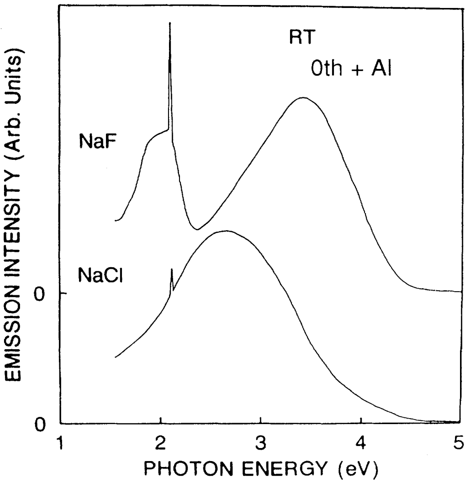

FIG. 1. Emission spectra of NaF and NaCl excited with zeroth-order light through an aluminum filter.

the response time of the slow component by using a mechanical chopper, and found that the response time is faster than 3 ms. This indicates that the slow component has a response time between 178 ns and 3 ms.

One might assume that two components in the time response of PSD are attributable to valence-band and core-level excitations, respectively. In order to confirm this assumption, we have measured the time response of PSD of excited-state sodium atoms from the NaF surface with valence-band excitation. The result, which has been derived in the same way as mentioned above, is shown in Fig. 4. The energy of 27 eV is far below the threshold of core-level excitation [32.5 eV (Ref. 8)]. As seen in this figure, the time response of PSD with valence-band excitation consists of two components. Therefore, it is concluded that two components in the time response of PSD do not correspond to valence-band and core-level excitations, respectively. We propose here that there are two PSD mechanisms with different response time for both valence-band and core-level excitations.[9]

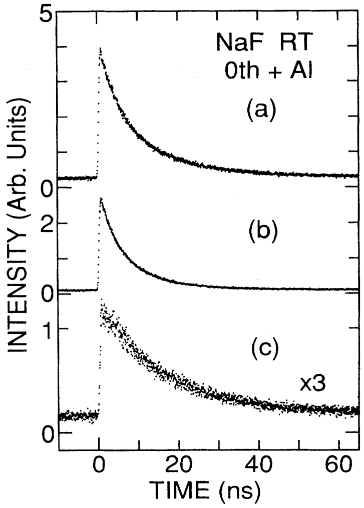

FIG. 2. Decay curves of the 2.10-eV emission of NaF. Curves (*a*), (*b*), and (*c*) are the observed decay at 2.10 eV, the decay of broad band, and the time response of excited-state alkali desorption, respectively.

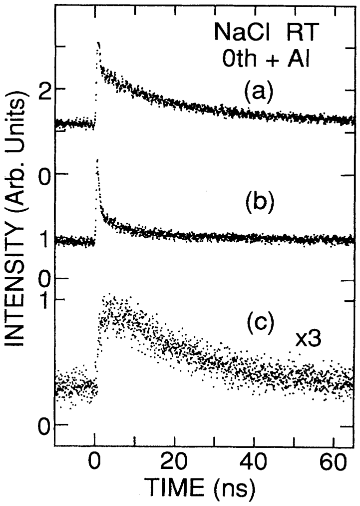

FIG. 3. Decay curves of the 2.10-eV emission of NaCl. Curves (*a*), (*b*), and (*c*) are the observed decay at 2.10 eV, the decay of broad band, and the time response of excited-state alkali desorption, respectively.

According to previous studies,[10–13] desorptions of halogen and alkali atoms in the ground state are considered to be due to the following processes, although the details are still unknown. (1) The photon beam deposits energy to produce electron-hole pairs. The holes are self-trapped to form V_K centers (the V_K center is a halogen$_2^-$ molecular ion located in two halogen sites with reduced interatomic distance). The electrons are captured by the V_K centers to form STE's. (2) The STE's can decay by inducing a replacement-collision sequence along the ⟨110⟩ direction leading to the formation of F and H centers (the F center is an electron trapped in a halogen vacancy and the H center is a halogen$_2^-$ molecular ion substituted at a halogen ion site). If the creation of initial STE's occurs so close to the surface that the range of replacement-collision sequence extends beyond the surface, halogen atoms are ejected from the crystal surface. (3) Besides this prompt emission, the delayed emission of halogen atoms can occur due to the diffusion of V_K centers or H centers from the bulk to the surface. (4) The remaining F centers diffuse to the surface and react with

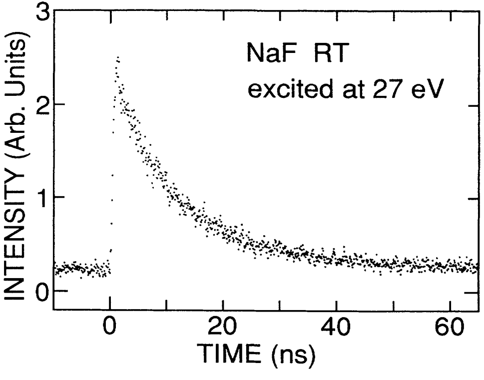

FIG. 4. The time response of excited-state alkali desorption from NaF excited at 27 eV.

alkali ions, resulting in neutral alkali atoms in the surface layer. (5) The alkali atoms evaporate thermally from the crystal surface.

The time response of ground-state halogen and alkali desorptions has already been reported. Loubriel *et al.*[11] and Green *et al.*[12] have measured the time response of ground-state Li desorption from LiF by using a pulsed electron beam, and found a response time in the μs to ms range. They suggested that the time response of ground-state alkali desorption is due to the thermal diffusion of F centers and their reaction with alkali ions in the surface layer. On the other hand, Kanzaki and Mori[13] have measured PSD of ground-state halogen and alkali atoms from RbBr and KI by using a mechanical chopper. They derived the time response of halogen and alkali desorptions to be in the submicrosecond range from the frequency dependence of the intensity obtained with a mass spectrometer. They suggested that the time response of halogen desorption is restricted by the lifetime of V_K centers diffusing to the surface through intermittent capture at point defects, and that the alkali desorption occurs via F centers near the surface.

Haglund *et al.*[7] have tried to see the time response of PSD of excited-state lithium atoms from LiF, but their attempts were not successful because their exciting photon pulse had a broad width and short interval. They also tried to measure the time response of electron-stimulated desorption (ESD) of excited-state lithium atoms from LiF at 400 °C by using a pulsed electron beam. Since the fluorescence signal turned off instantaneously when the electron beam was removed, they supposed from the best time resolution possible with their multichannel analyzer that the ESD signal of excited-state lithium atoms from LiF decreases within 0.1 μs. The ESD of excited-state alkali atoms at high temperatures is interpreted in terms of a gas-phase collision mechanism,[14] where desorbed ground-state alkali atoms interact collisionally with primary and secondary electrons to produce excited-state alkali atoms. However, this mechanism cannot be applied to the PSD of excited-state alkali atoms, since the ESD at high temperatures shows the incident-flux dependence which is different from that of the PSD.[5,15]

The present authors[5] have reported that desorption of excited-state alkali atoms is observed in the substances which have a large Rabin-Klick (RK) parameter (the RK parameter is the ratio of the space between adjacent halogen ions along $\langle 110 \rangle$ direction and the diameter of the halogen atom[16]). According to Overeijnder *et al.*[17] the nonthermal halogen desorption is also observed on alkali halides which have a large RK parameter. Recently, Kan'no, Tanaka, and Hayashi[18] have studied the intrinsic luminescence from alkali halides and discussed the relation of STE luminescence with RK parameters. They also proposed the existence of different types of STE's which depend on adiabatic potentials including the lattice distortion and displacement. These results indicate that the desorption process of excited-state alkali atoms is closely related to processes of defect formation, off-center distortion of the STE, and nonthermal halogen desorption.[19]

As seen in curves (c) of Figs. 2 and 3, the ratio of the integrated intensities between the fast and slow components is about 1:1 and 1:3 for NaF and NaCl, respectively, while the RK parameter of NaF and NaCl is 0.70 and 0.36, respecitvely.[16] This result indicates that the substance having a larger RK parameter shows a larger efficiency of fast desorption of excited-state alkali atoms. Therefore, we propose that the lattice instability at the electronic excited states in surface layers plays an important role on the fast PSD of excited-state alkali desorption, and that a precursor state producing the fast desorption of excited-state alkali atoms may be close to the off-center distorted STE (a kind of F-H pair) produced in the surface layer, which has a different environment from the bulk.

As shown in curves (c) of Figs. 2 and 3, and in Fig. 4 the PSD of excited-state Na desorption has the background which is due to a slow component. The response time of the slow component is in the time range from 178 ns to 3 ms, although it could not be definitely determined because of the experimental conditions mentioned above. This response time is in the same range as those of ground-state alkali and halogen desorptions. One might imagine that the slow desorption of excited-state alkali atoms are produced in the same way as the desorption of ground-state alkali atoms, but this is not exact. As reported previously,[5] the desorption yield of ground-state Na atoms from NaCl increases as the temperature is increased, while that of excited-state Na desorption has a maximum around room temperature. Moreover, the excited-state alkali desorption is observed in the substances which have STE's of an off-center type, high efficiency of coloration, and a large RK parameter, while the desorption of ground-state alkali atoms shows the reverse substance dependence. Therefore we propose that the slow desorption of excited-state Na atoms is due to the thermal instability of surface defects, which are different from those concerning the ground-state alkali desorption. At this stage, however, it is not clear what kinds of surface defects play important roles on the slow desorption.

In summary, we reported a successful observation of the time reponse of excited-state alkali desorption from NaF and NaCl by using synchrotron radiation pulses. It was found that the time response of PSD for excited-state alkali atoms consists of two components: the fast component in the ns range and the slow one between 178 ns and 3 ms. It was proposed that the fast component is due to the lattice instability induced by electronic excitation in the surface layer, while the slow component is attributed to the thermal instability of surface defects. In order to confirm this PSD mechanism, further investigations such as the temperature dependence of the time response are in progress.

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[1] See, for example, *Desorption Induced by Eelectronic Transitions DIET IV,* edited by G. Betz and P. Varga (Springer-Verlag, Berlin, 1989).

[2] N. H. Tolk, M. M. Traum, J. S. Kraus, T. R. Pian, W. E. Collins, N. G. Stoffel, and G. Margaritondo, Phys. Rev. Lett. **49**, 812 (1982).

[3] P. H. Bunton, R. F. Haglund, Jr., D. Liu, and N. H. Tolk, Surf. Sci. **243**, 227 (1991).

[4] P. H. Bunton, R. F. Haglund, Jr., D. Liu, and N. H. Tolk, Phys. Rev. B **45**, 4566 (1992).

[5] S. Hirose and M. Kamada, J. Phys. Soc. Jpn. **60**, 4374 (1991).

[6] D. Liu, N. Seifert, D. J. McClure, A. V. Barnes, R. G. Albridge, and N. H. Tolk, Phys. Rev. B **47**, 1553 (1993).

[7] R. F. Haglund, Jr., N. H. Tolk, G. M. Loubriel, and R. A. Rosenberg, Nucl. Instrum. Methods B **18**, 549 (1987).

[8] M. Kamada, O. Aita, K. Ichikawa, and K. Tsutsumi, Phys. Rev. B **36**, 4962 (1987).

[9] Strictly speaking, the present result does not exclude another possibility that the entire time structure might be explained by a single mechanism, if it leads to an initial fast fall in 60 ns and a long tail persisting in the time range above 178 ns. However, there are two types of mobile species, intrinsic defects and free carriers, in the surface layers after photon excitation. Thermal diffusion of the intrinsic defects and their reaction on sample surfaces occurs in the time range of μs to ms, while the free carriers diffuse in the time range of ps to ns to produce STE's. These facts make us consider two types of PSD mechanism.

[10] N. Itoh, Surf. Sci. **217**, 573 (1989).

[11] G. M. Loubriel, T. A. Green, P. M. Richards, N. H. Tolk, R. H. Albridge, R. F. Haglund, K. J. Snowden, L. T. Hudson, D. W. Cherry, R. K. Cole, M. H. Mendenhall, D. M. Newns, and P. M. Savundararaj, Phys. Rev. Lett. **57**, 1781 (1986).

[12] T. A. Green, G. M. Loubriel, P. M. Richards, N. H. Tolk, and R. F. Haglund, Jr., Phys. Rev. B **35**, 781 (1987).

[13] H. Kanzaki, and T. Mori, Phys. Rev. B **29**, 3573 (1984).

[14] R. E. Walkup, Ph. Avouris, and A. P. Ghosh, Phys. Rev. Lett. **57**, 2227 (1986).

[15] M. Kamada and E. T. Arakawa, J. Vac. Sci. Technol. A **8**, 3152 (1990).

[16] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[17] H. Overeijnder, M. Szymonski, A. Haring, and A. E. De Vries, Radiat. Effects **36**, 63 (1978).

[18] K. Kan'no, K. Tanaka, and T. Hayashi, Rev. Solid State Sci. **4**, 383 (1990).

[19] K. S. Song and R. T. Williams, *Self-Trapped Exciton,* Springer Series in Solid State Science Vol. 105 (Springer-Verlag, Berlin, 1993).