Emission of Na atoms from undamaged and slightly damaged NaCl (100) surfaces by electronic excitation

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We have carried out high-sensitivity measurements of the emission of Na atoms induced by irradiation with μs electron pulses of unirradiated NaCl (100) surfaces and with ns laser pulses of the NaCl (100) surfaces preirradiated with electrons. Similar to the results of ion bombardment, irradiation with an electron pulse is found to cause spontaneous emission of Na atoms with observable delays below 100 °C. It is found also that irradiation with a ns laser pulse of the preirradiated surface causes emission of Na atoms. The excitation spectrum for the laser-induced emission shows a peak near the *F*-band maximum. The yields of both the initial electron-pulse-induced emission and laser-induced emission on preirradiated surface are found to be reduced as the surface is damaged.

I. INTRODUCTION

Electronic excitation in the bulk of solids with strong electron-lattice coupling produces Frenkel pairs, while that on surfaces induces atomic emissions.[1] These phenomena originate from formation of electron-hole pairs or of excitons, of which the interaction with lattice leads ultimately to the local lattice rearrangement.[2] So far a great deal of work has been carried out on the deexcitation of electron-hole pairs and excitons in the bulk, and on the consequent defect formation.[3-5] It has been well established that an exciton in alkali halides is relaxed into a self-trapped exciton, which comprises a halogen molecular ion (X_2^- where X is a halogen atom) and an electron (see Fig. 1), and then further into a Frenkel pair in the halogen sublattice.

Contrary to the relaxation processes in the bulk, the understanding of the relaxation processes of an exciton and of an electron-hole pair on surfaces is still limited. Experimentally, it is known that the surface is alkali-enriched by electronic excitation:[6-9] thus, the emission of halogen atoms is considered to be primary.[10-13] Recent experimental observation that the nonthermal component in the velocity distribution of emitted atoms is observed only for halogen atoms supports this conjecture strongly.[14,15] Theoretical calculations by Puchin, Shluger, and Itoh[16] and Li, Beck, and Whetten[7] have shown that an exciton on the topmost surface relaxes into an *F* center on the topmost surface and an emitted halogen atom. Puchin, Shluger, and Itoh[16] have simulated the relaxation process of an exciton produced below the second layer and have found that it is converted to a self-trapped exciton and then to an *F* center near the surface and an emitted halogen atom. In any case, *F* centers are considered to be produced on the surface as a result of deexcitation of excitons. Electron-hole pairs near the surface will be converted to either excitons or pairs of an electron and a self-trapped hole. These pairs are recombined to self-trapped excitons. Thus, the consequence of the production of the electron-hole pairs is similar to that of excitons.

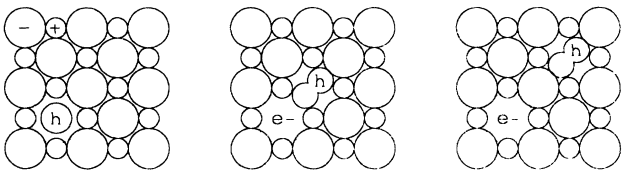

FIG. 1. A Schematic diagram of the relaxation of an exciton in alkali halides: (a) an unrelaxed exciton, (b) a self-trapped exciton, and (c) a pair comprising an *F* center (a halogen vacancy) and an *H* center (an interstitial halogen atom). *e* denotes an electron, *h* denotes a hole, and a double circle denotes a halogen molecular ion.

Alkali atoms are also known to be emitted under ionizing irradiation, either at the ground state[18,19] or at an excited state,[20,21] but the mechanism of alkali emissions is not yet clear. The most fundamental question has not been solved yet: is the emission of alkali atoms a result of exciton relaxation and is it accompanied with the halogen emission upon exciton relaxation, or is it a secondary process arising from the remaining *F* centers? The experimental results that the surface becomes alkali rich[6-9] as ionizing irradiation is continued indicate that the number of emitted halogen atoms exceeds the number of emitted alkali atoms. This supports the conjecture that halogen emission is primary, although it is not yet clear whether an alkali atom can be emitted as a result of relaxation of an exciton.

If the emission of alkali atoms is a secondary process due to nonstoichiometric emission from the halogen sublattice, two fundamental different causes for alkali emission are conceivable: photoexcitation or thermal evaporation. There are two extreme cases for each process; one is from surface *F* centers and the other from metallic colloids, although intermediate cases may be effective as well. According to Puchin, Shluger, and Itoh,[16] the Na atoms neighboring an *F* center in NaCl are stable at the ground state of the *F* center, but electronic excitation of the *F* center to the next higher *p* orbital produces an antibonding state for a Na atom. Experimental verification for this process has not yet been obtained. The clusters of the surface *F* centers, or metallic precipitate of alkali

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atoms, are believed to be evaporated thermally around 100 °C,[22] but the effects of electronic excitation on the metallic precipitate is not known.

One of the experimental problems of sputtering or atomic emissions induced by radiation is the radiation damage introduced in the process of measurement. Even if the surface is well characterized at the start of a measurement, the surface is progressively damaged during the measurement. Thus, the results obtained in an experiment may include the response of not only undamaged but also damaged surfaces. A recent investigation of the emission of alkali atoms using the laser-induced fluorescence has indicated that the emission yield of alkali atoms is reduced, and the emission of excited alkali atoms is increased as the surface is damaged.[23–25] These results indicate that the consequence of the interaction of electronic excitation with the surface depends strongly on the surface damage.

In order to deal with the exciton relaxation on surfaces, the atomic emission from undamaged surfaces should be clarified. For this purpose it is necessary to carry out high-sensitivity measurements of atomic emissions from clean surfaces; the sensitivity of the detector should be high enough not to modify the surface substantially during measurements. Resonance-ionization spectroscopy (RIS) has been successfully used for measurements of ion-induced[26] and laser-induced[27] sputtering or atomic emissions. Postawa *et al.*[28] have carried out RIS measurements of ion-induced emission of Na atoms from the NaCl (100) surfaces and found two components, one emitted within 1 μs and the other with a delay of about 10 μs below 100 °C. Although their experimental results are considered to be the consequence of the interaction of the electronic excitation with surfaces, unfortunately, the degree of damage and the correlation between the emission and the surface damage is not clarified. Furthermore, irradiation by ion beams induces elastic encounters to a certain degree. Thus, carefully designed experiments using electron and photon beams are necessary.

The present paper reports RIS measurements of the emissions of Na atoms by electron irradiation of the cleaved NaCl (100) surface, purely the effects of electronic excitation of clean surfaces. The emission of alkali atoms induced by irradiation with an electron pulse was obtained, as was that with laser pulses following an electron pulse. The former gives information on the alkali emission induced by an electron pulse and the latter on the products left on the surface after electron-pulse irradiation. It is found that alkali atoms are emitted by irradiation with an electron pulse as well as by laser pulses following an electron pulse. Measurements of the excitation spectrum for laser-induced emission after electron-pulse irradiation revealed that the F centers are left on the surface and Na atoms are emitted by photoexcitation of the F centers. The effects of the surface damage on the emission of Na atom are also studied.

II. EXPERIMENTAL TECHNIQUE

Specimens of NaCl crystals cleaved in air from a block purchased from Horiba were placed on a sample holder in an ultrahigh vacuum chamber, of which the base vacuum is 5×10^{-8} Pa. 400-eV electron pulses were generated using a conventional electron gun. For measurements of the emission of Na atoms, electron pulses of a width of 1 μs and of a current density of 100 μA/cm^2 were used. The same electron source was used for preirradiation; in this case, repeated irradiation with electron pulses of durations between 1 μs and 1 ms or continuous irradiation was employed. For measuring the emission from damaged surfaces, 28-ns excimer-pumped dye-laser pulses were used. The wavelength of the laser photons was changed from 440 to 600 nm and the fluence of laser beams was in a range between 10 μJ/cm^2 and 10 mJ/cm^2, and was changed by placing a neutral-density filter in the optical path.

Na atoms emitted were detected using the RIS technique: the emitted atoms were excited by a 330.3-nm pulsed laser beam, a frequency-doubled dye-laser beam, and then ionized by the fundamental dye-laser beam. The fundamental and frequency-doubled laser beams travel in parallel to the specimen surface at a distance between 2 and 5 mm from the specimen surface. Na ions were collected on a channeltron, of which output current was stored in a computer. By this technique, Na ions of about 10^{-6} monolayer can be detected. In obtaining the time delay in the emission, a time-of-flight (TOF) technique was employed by changing the time interval between the pump beam to produce the emissions and the probe beam to ionize the emitted atoms.

III. EXPERIMENTAL RESULTS

A. Emission of alkali atoms induced by electron pulses

We found that irradiation of the clean NaCl (100) surface with a 100-μA/cm^2 electron pulse of a duration of 1 μs produces a detectable emission of Na atoms from the very beginning of irradiation. In order to reveal whether the emission of alkali atoms is defect related, we measured the emission yield induced by an electron pulse as a function of the preexposure electron dose. To obtain the effect of irradiation below a total exposure of 100 nC/cm^2, we measured the change in the emission yield induced by a 100-μA/cm^2 electron pulse of 1-μs duration as a specimen was irradiated repeatedly. For higher exposures, the specimen was irradiated for a fixed time period with a 100-μA/cm^2 electron beam and then the emission yield by a 1-μs pulse was measured. As shown in Fig. 2(a), no change in the emission yield occurs for the exposure less than 40 nC/cm^2, while the prolonged irradiation reduces the Na yield [Fig. 2(b)]. This result excludes the possibility that emission of Na atoms originates from the stoichiometry change induced by irradiation. Since each electron produces the emission of only a few atoms[10] and only 10^9 electrons/cm^2 are incident in each electron pulse, the result above indicates clearly that the emission of alkali atoms is a consequence of irradiation with an electron pulse of undamaged sites. Furthermore, the probability that the same spot on the surface is hit by two electrons within the same electron pulse is extremely small in this fluence. Thus, emission of alkali

atoms is a consequence of the incidence of an electron pulse on an undamaged spot.

According to measurements of ion-induced emissions by Postawa *et al.*,[28] a delayed emission was observed below 100 °C. In order to see whether the same delayed emission occurs for electron irradiation, we carried out TOF measurements of emitted Na atoms induced by an electron pulse between 20 and 300 °C. Typical results are shown in Fig. 3. Evidently the TOF spectrum is represented by a Maxwell-Boltzmann distribution at 120 °C [Fig. 3(a)], but a delayed component was observed at 80 °C [Fig. 3(b)]. The results are similar to those obtained by Postawa *et al.*:[28] the Maxwellian distribution was obtained above 120 °C and the delay times at lower temperatures obtained by Postawa and by present experiments are almost identical. Combining this with the results of Fig. 2, the delay in the emission is a consequence of the interaction of an incident electron with the undamaged surface.

The temperature dependence of the yield was measured in the temperature range where the delayed component does not appear. As shown in Fig. 4, the yield is almost independent of temperature. This result contrasts the previous measurements of sputtering that had been carried out at a condition where the surface is damaged during the measurements.[22]

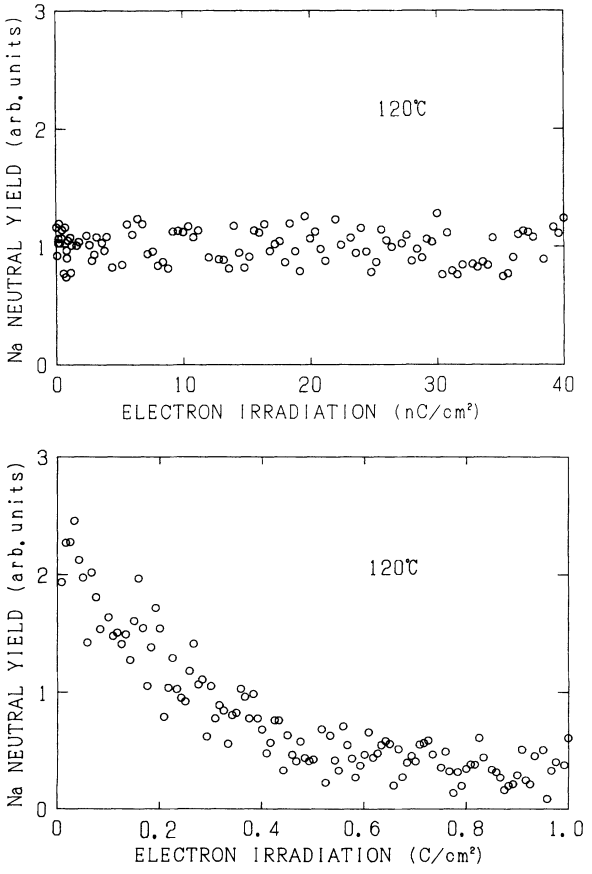

FIG. 2. The effect of irradiation with electrons on the emission yield of Na atoms induced by irradiation of NaCl with a 100-μA/cm^2 electron pulse of 1-μs duration at 120 °C; (a) for low-irradiation dose and (b) for high-irradiation dose.

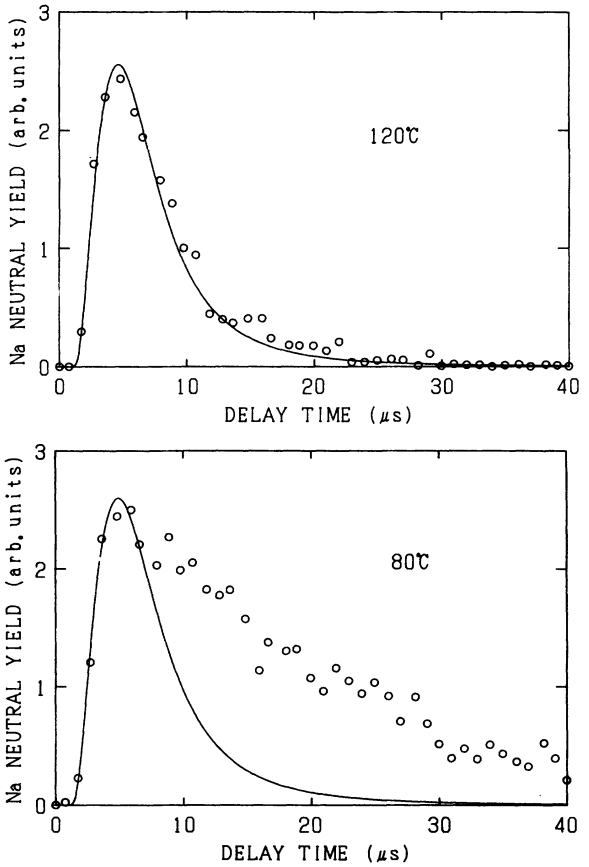

FIG. 3. TOF spectra of Na atoms emitted by irradiation of the NaCl (100) surface with a 100-μA/cm^2 electron pulse of 1-μs duration at (a) 120 °C and (b) 80 °C.

B. Emission of Na atoms induced by laser pulses following electron irradiation

Although the emission of Na atoms is induced upon incidence of each electron pulse, it is also true that the surface is progressively damaged by bombardment with electron pulses. In order to examine the surface after each electron pulse, we measured the emission of Na atoms in-

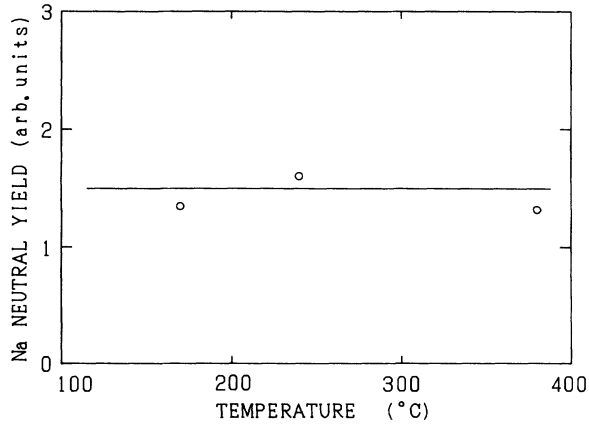

FIG. 4. The temperature dependence of the emission yield of Na atoms by irradiation with a 100-μA/cm^2 electron pulse of 1-μs duration of the NaCl (100) surface.

duced by laser irradiation after electron irradiation. Figure 5 shows the result for laser-induced emission after irradiation with an electron pulse of 1 $\mu C/cm^2$. The abscissa of the figure indicates the number of the 1-mJ/cm^2 laser pulses of 28-ns duration incident on the same preirradiated spot of the specimen. Evidently no emission is induced before electron irradiation. After electron irradiation, the repeated irradiation with laser pulses induces emission, which is gradually reduced to zero as the irradiation is repeated. This curve is typical for laser-induced emission initiated by defects on surfaces.[29] It is clear that the laser-induced emission from the predamaged surfaces is originated from the surface damage; the area under the curve, shown in Fig. 5, is indicative of the damage or local stoichiometry change induced by electron irradiation. As we will explain later, in fact the area under the curve is proportional to the electron dose below about 40 nC/cm^2.

In order to reveal the nature of the damage induced by electron pulses, we measured the excitation spectrum for the laser-induced emission. A specimen was previously irradiated with an electron beam by a dose of 1 $\mu C/cm^2$ and the number of laser-induced emitted alkali atoms per laser pulse of various photon energies at the initial stage of laser irradiation was measured at 120 °C. As show in Fig. 6, the excitation spectrum possesses a peak at 2.6 eV and is similar to the F band at 120 °C, shown by the solid curve, obtained from existing data of the temperature dependence of the peak energy and half-width of the F center.[30] Although the error in the experimental results is relatively large, mainly due to the scattering of the intensity of the laser pulse, we see the trend that the yield takes a maximum near the F-band maximum. According to Puchin, Shluger, and Itoh,[16] the electronic transition energies of an F center on the (100) surface split into two: one nearly identical for the bulk F-center transition energy and the other shifted to lower energy by 0.2 eV. Thus, the emission of Na atoms induced by laser-pulse irradiation followed by electron-pulse irradiation is most likely to arise from electronic excitation of the F centers on the surface left after halogen emission.

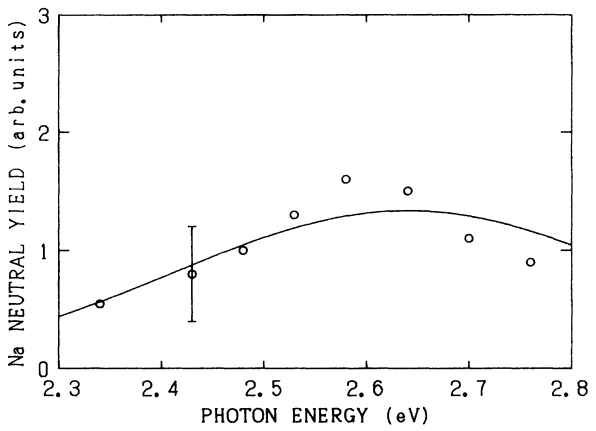

FIG. 6. The photon-energy dependence of the number of Na atoms emitted by irradiation with 28-ns laser pulses of the NaCl (100) surface preirradiated with electrons of a dose of 1 $\mu C/cm^2$ at 120 °C.

The relation between the yield of the laser-induced emission of slightly damaged surfaces and the laser fluence is linear, as shown in Fig. 7, indicating that the absorption of a single photon by an F center can lead to the emission of a Na atom. The experimental results that the laser pulses after the electron-pulse irradiation induce emission of Na atoms indicate that electron-pulse irradiation induces F-center production at the surface besides the Na emissions. It follows that an electron pulse induces emission of both Cl and Na atoms; the former is more numerous than the latter.

We measured the temperature dependence of the yield of the Na emission induced by laser pulses following electron irradiation in the following way. First, the specimen was irradiated with electrons with an exposure of 1 $\mu C/cm^2$ at several temperatures and then irradiated with laser beams until laser-induced emission is eliminated. The total number of Na atoms emitted by laser pulses is plotted as a function of the temperature in Fig. 8. Evidently, the yield is independent of temperature below

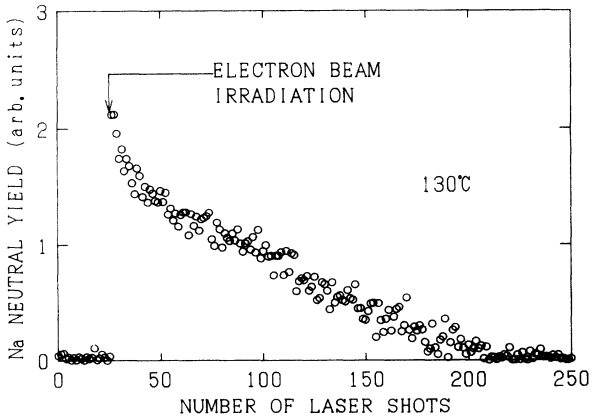

FIG. 5. The number-of-shot dependence of the emission yield of Na atoms induced by irradiation with a 1-mJ/cm^2 laser pulse of 28-μs duration of the NaCl (100) surface preirradiated with electrons of a dose of 1 $\mu C/cm^2$.

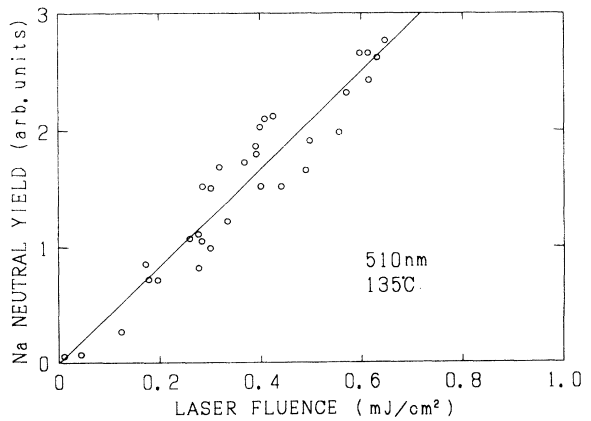

FIG. 7. The laser-fluence dependence of the total number of Na atoms emitted by repeated irradiation with 28-ns laser pulses of the NaCl (100) surface preirradiated with electrons of a dose of 1 $\mu C/cm^2$ at 135 °C.

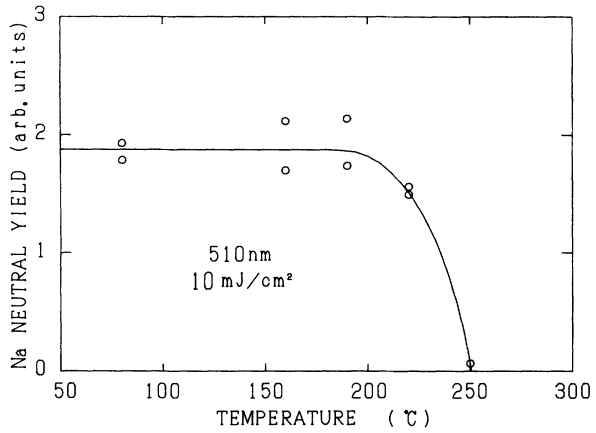

FIG. 8. The temperature dependence of the total number of Na atoms emitted by repeated irradiation of the NaCl (100) surface preirradiated with electrons of a dose of 1 $\mu C/cm^2$ measured with 28-ns laser pulses of 510 nm in wavelength.

200 °C, above which it decreases, probably because of the instability of the F centers. The result indicates that the F centers at the surface are stable below 200 °C. The result also indicates that not only the yield of Na atoms emitted by an electron pulse, but also the number of excess Na atoms (the F centers on the surface) left after an electron pulse, are independent of temperature.

The total number of Na atoms emitted by repeated laser pulses after electron irradiation, namely the number of the F centers produced by an electron pulse, is plotted as a function of electron dose in Fig. 9. The ordinate of the figure is indicative of the radiation damage caused by electron irradiation. Clearly the result exhibits a saturation curve, indicating that the yield of the F centers is reduced as the radiation damage is accumulated on the surface. The first derivative of the curve at the initial linear stage indicates the number of alkali atoms accumulated by unit exposure, namely the number of halogen atoms emitted by an electron pulse not accompanied with the spontaneous Na emissions within the pulse. The deviation from the linear relation can be ascribed to the effects

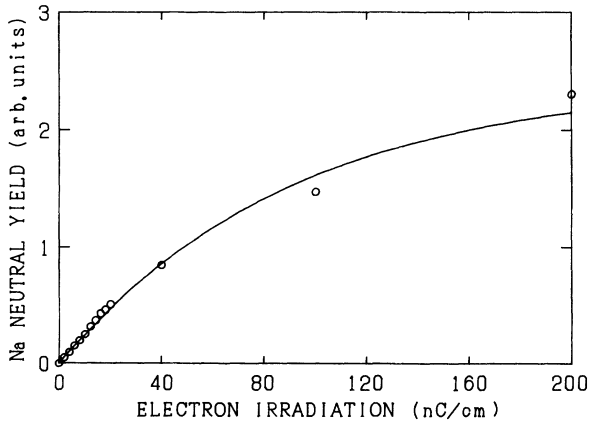

FIG. 9. The total number of Na atoms emitted by repeated irradiation of the NaCl (100) surface preirradiated with electrons of doses between 1 and 200 nC/m^2, measured with 28-ns laser pulses of 470-nm wavelength.

of radiation damage, which reduces either the yield of the Na emission because of the interaction between the F centers left on the surface or the yield of halogen emission. We discuss this point later.

The measurements were made for the delay of Na emissions induced by laser irradiation of the damaged surfaces below 80 °C. Almost the same delay was observed as that observed after electron irradiation. Thus, it appears that the mechanism of the emission of alkali atoms induced by irradiation with an electron pulse is the same as that induced by excitation of the F centers.

IV. DISCUSSION

A. Discussion on the consequence of electronic excitation on undamaged surface

From the present experimental results, it is clear that the incidence of an electron induces the emissions of both halogen atoms and alkali atoms; the latter is less numerous. Because of the difficulty of the quantitative evaluation of the number of Na atoms emitted by an electron pulse and the number of Na atoms left after an electron pulse, we did not make a further effort to obtain the absolute ratio for the emissions of a halogen atom with and without the accompanied emission of an alkali atom.

According to the present experimental results, the yield of the emission of Na atoms induced by an electron pulse is independent of temperature between 80 and 400 °C. Furthermore, the yield of the emission of Cl atoms not accompanied with the emission of Na atoms is also found to be constant between 50 and 200 °C. The total yield of the halogen atoms, which is the summation of the two, is temperature independent at least within the two overlapping temperature ranges, between 80 and 200 °C. This result is strongly contrasted to the temperature dependence of the erosion of NaCl obtained by Townsend and co-workers[7,22] without much attention on the surface damage. These authors observed an increase in the yield of halogen and alkali with an activation energy of 0.23 eV and ascribed it to the vaporization of excess alkali on the surface. The absence of the temperature dependence obtained in the present experiments indicates that the yield of the emission of halogen atoms due to annihilation of the excitons on the surface is independent of temperature. The result is consistent with the theoretical result by Puchin, Shluger,and Itoh,[16] that an exciton on the surface is antibonding with respect to a halogen atom on the surface.

The absence of the temperature dependence may be correlated with the experimental results by Koloziej *et al.*[31] that the yield of the nonthermal component of emitted Br atoms from KBr is weakly dependent on temperature; only a slight decrease is observed as the temperature increases. The fast component, considered to arise from dynamic relaxation of an exciton,[32] may be less dependent on the secondary processes.

B. The mechanism of the emission of alkali atoms

Two mechanisms of the emission of Na atoms induced by an electron pulse are conceivable; one due to the exci-

tonic process, namely the emission of an alkali atom and/or halogen atom as a result of exciton relaxation, and the other due to the excitation of the F centers. Since the Na emission can be observed for a dose of 0.1 nC/cm^2, for which the number of incident electrons is only 10^{-6} of the number of atoms on the surface, it is unlikely that the F centers produced by an incident electron are excited by another electron. Thus, if the second mechanism is effective, we should assume that the electron-hole pairs produced by an incident electron should first create an F center on the surface and subsequently excite the F center during their lifetime. The emission of both alkali and halogen atoms from an exciton is energetically possible according to the calculation by Puchin, Shluger, and Itoh:[16] an extra energy of about 2 eV remains after the emission of a halogen atom by the relaxation of an exciton, and about 2 eV is required to remove a Na atom from the nearest neighbor of an F center at the ground state. Alternatively, it is also plausible that either a halogen atom or an alkali atom is emitted by creation of an exciton or an electron-hole pair; the branching may depend on the relaxation channel or the position that an exciton is created with respect to the surface. Thus, it is not yet clear which mechanism is the cause of the emission of alkali.

The present experimental results that almost the same delay is observed for the emission of Na atoms by irradiation with an electron pulse and by irradiation with a laser pulse of the damaged surface are in favor of, but not conclusively, the second mechanism. In order to show whether this mechanism is effective, it is necessary to carry out experiments of photon-induced emission of an undamaged surface. If the first mechanism is effective, the emission yield should be proportional to the number of excitation, while if the second mechanism is effective, it should be proportional to the product of the intensities of the photon beam that induces band-to-band excitation and that excites the F centers.

C. Effects of surface damage on the Na emission induced by electronic excitation

According to the present investigation, irradiation of the clean surface of NaCl induces the emissions of Na atoms and formation of F centers near surfaces. If we take the number of Na atoms emitted by electron irradiation of dose x as $n_1(x)$ and the number of the F centers accumulated on the surface as $n_2(x)$, the number $n(x)$ of the halogen atoms emitted may be given by

$$n(x)=n_1(x)+n_2(x) . \tag{1}$$

The number of halogen atoms emitted from undamaged surfaces may be given by

$$\frac{dn}{dx}=\alpha-\beta n , \tag{2}$$

where α is the production rate per unit does, and β is a parameter that describes the reduction of the emission yield because of formation of the F centers on the surface. As far as the surface is not damaged, $n_1(x)$ and $n_2(x)$ are considered to take the same functional form. Using Fig. 9, which indicates a growth curve for $n_2(x)$, we found that $\beta=0.84\times10^7$ cm^2/C. It follows that the saturation starts to occur after incidence of about 10^{12} electrons per cm^2. The average distance between two incident electrons on the surface at the saturation level is about 30 lattice constant. We presume that the excitons or electron-hole pairs on the surface can migrate by this distance and recombine by interacting F centers without inducing emissions.

We found that the growth curve for $n_2(x)$ deviates from the saturation curve shown in Eq. (2). The reason is probably formation of clustered F centers or Na atoms. Similarly we found that $n_1(x)$, which is the integral of the curve shown in Fig. 2(b), does not show a simple exponential curve. Besides the low-electron-dose region where both $n_1(x)$ and $n_2(x)$ are linear, the $n_1(x)$ and $n_2(x)$ will show complex functional form different from each other. We did not make further detailed comparisons of these two functions experimentally.

In conclusion, we studied the response of the cleaved NaCl (100) surface with electron beams and found the emission of Na atoms and formation of the defects, which can be the source of the emission of alkali atoms. These defects are most likely the F centers. The yields of these processes are found to be reduced by the damage of the surface. Although surfaces cleaved in air were used in the present experiment, the effect of contamination was not observed: the emission yield of Na atoms was not altered as irradiation was repeated. Most probably the trace adsorbates are evaporated as the specimen was kept in a high vacuum. It is of interest to carry out similar experiments for vacuum-cleaved specimens and to study the effects of adsorbates on these surfaces.

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